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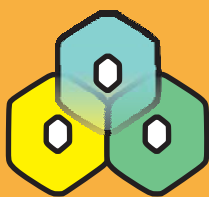
# ACTA

## MINERALOGICA-PETROGRAPHICA

### ABSTRACT SERIES

**Volume 8**

**2014**



*5<sup>th</sup> ISGC  
Budapest  
Hungary*

5<sup>th</sup> International Students Geological  
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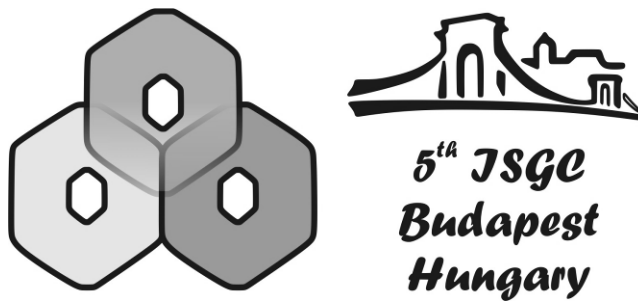
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## **Chemical compaction of overpressured shales**

**Péter András, Andrew Aplin, Neil Goulty, Stuart Jones**

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Accurate pore pressure prediction is essential for well planning. Direct pore pressure measurements may be available from permeable reservoir formations. In mudrock sequences pore pressures can only be estimated indirectly, by empirical methods from seismic reflection data and wireline log responses.

In low temperature environments pore pressures can be estimated from porosity assuming that porosity loss is entirely mechanical and is driven by vertical effective stress according to Terzaghi's Principle. By establishing relationships between porosity and vertical effective stress for mechanically consolidated mudstones, pore pressure can be estimated from vertical stress (overburden thickness) and measured or log-inferred porosities.

In higher temperature environments, methods based on a porosity-effective stress relationship fail to deliver accurate pressure predictions. This is because in the deeper and hotter parts of basins porosity reduction continues due to chemical rather than mechanical compaction processes, and leads to underestimation of pore pressure. Temperature affects the kinetics and equilibrium of chemical processes; it causes mineral transformations, grain dissolution and cementation. The porosity-effective stress methods

for estimating pore pressure must be used with extreme caution where siliciclastic or biogenic mudstones have been subjected to temperature-related mineralogical changes.

The overall objective of this project is to investigate the link between chemical compaction, the consolidation state of mudrocks and their physical properties as determined by wireline logs. We have selected three suites of samples, one from the Lower Cretaceous offshore mid-Norway, one from the Triassic of the Central Graben, North Sea and one from the Malay Basin offshore Peninsular Malaysia, all of which have undergone chemical diagenesis in a range of pore pressure environments. A set of different methodologies including XRD, SEM, EDX, SEM CL, FIB SEM, HRXTG, and MICP will be applied to describe the composition, texture and physical properties of mudstone samples. Results will allow us to test the extent to which mineralogical changes lead to porosity loss independent of pore pressure and the extent to which pore pressure signatures are retained by mudstone fabrics.

Funded by GeoPOP3 Industry Research Consortium.

## Composition, sources and differentiation mechanisms of magmas of Changbaishan Tianchi volcano (China-North Korea)

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In the Late Cenozoic, a large intraplate volcanic province was formed in the eastern part of the Asian continent. The province extends over a territory of 2500 x 2500 km<sup>2</sup> and its structure is defined by a number of autonomously evolving volcanic areas. Although these areas are spatially and structurally separated, their volcanic products are similar (these are predominantly lavas of elevated alkalinity), as also are the types of eruptions (predominantly fissure eruptions). The remarkable Changbaishan Tianchi volcanic area at the boundary between China and North Korea hosts four large stratovolcanoes, which differ from other volcanic edifices in the province not only by their shapes but also the composition of their rocks (which vary from basalt to rhyolite) and also in having widespread pyroclastic rocks: pumice, tuff, and ignimbrite. The most widely known volcano is Changbaishan Tianchi (known as Pektusan in Korea), which is made up mostly of trachyte and pantellerite.

We utilized our original geochemical data on rocks sampled during our fieldwork to estimate the composition of the parental magmas of Changbaishan Tianchi volcano and to get insight into the circumstances and mechanisms of their differentiation.

The geological evolution of Changbaishan Tianchi volcano comprises the following major stages: origin of the shield platform at 4.5 Ma (Liu *et al.*, 1998) and the formation of the volcanic cone and its caldera evolutionary stage, which ended with a catastrophic eruption at 939-946 A.D. (Wei *et al.*, 2013). Changbaishan Tianchi volcano is still active, a number of its historic eruptions were documented, the latest of which occurred approximately a century ago in 1903 (Wei *et al.*, 2013).

The rocks of the shield basement of Changbaishan Tianchi volcano vary from basalt to trachyandesite and typically contain the olivine-clinopyroxene-plagioclase assemblage. The cone of the volcano consists mostly of pyroclastic rocks of trachyte, comendite, and pantellerite composition that typically contain anorthoclase, quartz, clinopyroxene, and fayalite. The accessory minerals are ilmenite, titanomagnetite, and apatite. The slopes of the volcano are intruded by necks and dikes of alkali basalt, trachybasalt, and trachybasaltic andesite. Pantellerite vitrophyre bodies are exposed in the slopes around the caldera. The pyroclastic material of Changbaishan Tianchi volcano consists of trachybasaltic andesite bombs, which occur near basalt diatremes, and acid pumice, which compose the pyroclastic mantle on the slopes.

In the alkalis vs. silica diagram, the fields of the mafic and acid products are clearly separated from one another, thus accentuating the bimodal character of the magmatic rocks.

The lavas composing the shield platform of Changbaishan Tianchi volcano are weakly differentiated mafic rocks whose geochemical characteristics are generally similar. The rocks are characterized by low REE concentrations, with LREE strongly dominating over HREE ((La/Yb)<sub>N</sub> = 34 – 38). All of the rocks show weakly pronounced positive Eu anomalies, are enriched in Ba (up to 810 ppm in the basalt and trachybasalt, up to 2800 ppm in the trachybasaltic andesite, and up to 2960 ppm in the trachyandesite) and depleted in U.

We have examined the distribution of trace elements in the trachybasaltic andesite, trachyte, trachydacite, and rhyolite from the cone of Changbaishan Tianchi volcano. The trachybasaltic andesite exhibits fairly steeply inclined REE patterns ((La/Yb)<sub>N</sub> = 19 – 23) at relatively low REE concentrations. The trachybasaltic andesite is enriched in Ba (up to 800 ppm) and depleted in Th and U, whose concentrations are no higher than 100 ppm. The geochemistry of these rocks is similar to the geochemistry of the rocks composing the shield platform. All silicic rocks composing the cone of the volcano have conformable normalized trace-element patterns, and their (La/Yb)<sub>N</sub> = 15 – 23. The rocks show negative Eu anomalies, whose 'depths' are different for the trachyte, trachydacite, and rhyolite. The REE concentrations of these rocks are high and reach 1000 ppm. The silicic rocks are also noted for high Zr (up to 2340 ppm) and low Ba (usually <100 ppm) and Sr (no higher than 20 ppm) concentrations.

Geochemical data on rocks of Changbaishan Tianchi volcano reveal the following tendencies. The distribution of trace elements in basaltoid from this volcano is similar to that in OIB. The Changbaishan Tianchi basaltoids differs from the latter only in bearing higher concentrations of trace elements and REE. In the rock sequence from the basalt to pantellerite, the concentrations of REE (except Eu) and Zr increase, and those of Ba, Sr, and Eu decrease.

The Zr, Y, Ta, Hf, Th, and Rb concentrations in rocks of both the shield and the cone of the volcano were determined to be positively correlated with Nb, as also are REE (both HREE and LREE). This distribution of trace elements suggests that crystal fractionation played a leading role in producing the whole spectrum of rocks composing Changbaishan Tianchi volcano.

In order to estimate the sources from which the parental magmas of the volcano were derived, we used paired ratios of the most incompatible elements (Th/Yb – Ta/Yb, Zr/Nb – Nb/Th), because these ratios are only insignificantly modified in the course of magmatic differentiation. It was determined that data points of the Changbaishan Tianchi volcanic rocks generally (regardless of the petrographic compositions) compose a fairly compact group not far from the field of the OIB-type source. These common features of the rocks suggest that the composition of the magma source was highly homogeneous for the whole petrographic series of volcanic rocks.

The aforementioned geochemical patterns of the rocks indicate that the parental magmas were basalt of elevated alkalinity. The geochemistry of these melts is practically identical with that of OIB. Because of this, the magma source of Changbaishan Tianchi volcano should be compared with the mantle of close to the mantle of oceanic islands and generally to the magma source of the Late Cenozoic volcanic province in East Asia, i.e., with the mantle related to mantle plumes.

Liu, R., Fan, Q., Zheng, X., Zhang, M., Li, N. (1998): Sci in China (Series D), 41/4: 382–389.

Wei, H.Q., Liu, G.M., Gill, J. (2013): Bull Volcanol, 75/4:706–719.

## New petrographic and geochemical data on the upper mantle beneath the Styrian Basin (Austria and Slovenia)

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Alkali basaltic volcanism in the Carpathian-Pannonian Region (CPR) occurred sporadically across eastern Austria, northern Slovenia, Hungary, western Romania and southern Slovakia during Plio-Pleistocene times (Szabó *et al.*, 2004). Lavas and their pyroclasts often contain ultramafic xenoliths, and the majority of them have been extensively studied (e.g. Szabó *et al.*, 2004 and references therein), except the Styrian Basin Volcanic Field (SBVF, Eastern Austria). Geochemical and isotopic studies on the ultramafic xenoliths from the SB published are mostly focused on a few well-known volcanic centers (e.g., Kapfenstein & Tobaj) (e.g. Kurat *et al.*, 1980; Vaselli *et al.*, 1996; Falus *et al.*, 2000; Coltorti *et al.*, 2007; Dobosi *et al.*, 2010).

In this study new petrographic, textural and mineral chemistry data are presented on selected ultramafic xenoliths from three localities of the SBVF (Neuhaus, Güssing and Grad), which were not studied previously in details. The goals of this study are: i) to characterize the lithospheric mantle composition beneath the SBVF to a greater extent than in previous studies; ii) to assess whether SBVF lithospheric mantle was affected by geochemical processes similar to those observed in other ultramafic xenolith suites from the CPR.

Xenoliths have variable size, from 2-3 cm at Grad up to 5-8 cm at Güssing and Neuhaus. Spinel lherzolites, harzburgites are all present and there is a peculiar abundance of olivine-websterites. The orthopyroxene/clinopyroxene ratio in the suite shows a great variability (between 0.5 and 10) compared to the Phanerozoic subcontinental lithospheric mantle peridotites, which show values around 2 (Downes, 1997). In the xenoliths olivine is typically kink-banded, which is a sign of slight mantle deformation and ortho- and clinopyroxenes frequently show exsolution lamellae. Some of the samples contain minor interstitial amphibole.

The SBVF peridotite xenoliths have mostly protogranular, protogranular to porphyroclastic and porphyroclastic textures (Fig. 1). Pyroxenites, however, generally show a coarse-grained igneous texture. The textural distribution of the studied peridotite xenoliths is more variable compared to previously reported suites from the SBVF, originated basically from Kapfenstein.

The mg# number of the analysed olivines are ranging between 0.87 and 0.91, their NiO content varies between 0.18-0.37 wt. %. The CaO concentrations are between 0.02 and 0.10 wt. %.

The orthopyroxenes mg# numbers are varying between 0.89 and 0.92. Their Al<sub>2</sub>O<sub>3</sub> content is between 1.80 and 5.72 wt. %. The mg# number of clinopyroxenes are varying between 0.84 and 0.94. The cr# (0.10-0.37) and mg# (0.63-0.81) number of the spinels are showing great variability. All of the samples, except one sample from Güssing, are within the olivine-spinel mantle array (OSMA, Arai, 1987), which suggest only little mantle metasomatism, based on major element geochemistry. Based on their clinopyroxene and spinel major element geochemistry, two xenoliths from Neuhaus are the most depleted ones, with low Al<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O and high Cr<sub>2</sub>O<sub>3</sub> content.

The analysed amphiboles have 0.7-0.89 mg# number, and are pargasite and hastingsites. Their Na<sub>2</sub>O and TiO<sub>2</sub> contents are varied, the Grad xenoliths are more depleted in Na<sub>2</sub>O, and richer in TiO<sub>2</sub>, compared to the Güssing samples.

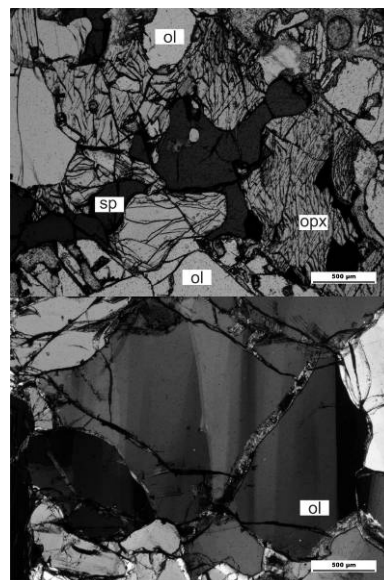


Fig. 1.: Upper: Protogranular texture, with a typical spinel-orthopyroxene cluster (Güssing 2 xenolith, 1N); Lower: Porphyroclastic texture, with kink bands in an olivine porphyroclast (Neuhaus 1 xenolith, +N).

Preliminary results show that the lithospheric mantle beneath the SBVF can be considered to be more deformed than previously thought (e.g. Dobosi *et al.*, 2010). Although the SBVF was thought to be dominated by depleted and underformed peridotites based on the previous studies (e.g. Kurat *et al.*, 1980) focusing mostly on Kapfenstein locality, the enrichment by metasomatic agents have been proved by the presence of ortho- and clinopyroxene rich rocks, as well as the appearance of amphiboles. On a regional scale, the SBVF lithospheric mantle can be compared to the other volcanic fields in the CPR (Szabó *et al.*, 2004) that went through extensive mantle metasomatism.

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 Vaselli, O., Downes, H., Thirlwall, M., Dobosi, G., Coradossi, N., Seghedi, I., Vannucci, R. (1995): J of Petrol, 36: 23-53

## Thermochronology of the Recsk Igneous Complex, NE-Hungary

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Most of the Alpine subduction related Paleogene magmatic complexes are located along the Periadriatic Lineament (Exner, 1976); the Recsk Paleogene volcanic centre is the northeasternmost endmember of these. The Recsk Complex is unique, since the Paleogene volcanic edifice is well preserved and the intrusive-volcanic assemblage hosts various ore deposits (Földessy & Szebényi, 2008). The evolution of this area is complex, because the Mátra Mountains, a significant volcano covered the Paleogene magmatic system in the Middle Miocene. It is assumed, that the thermal heating induced by the Mátra volcano, affected the adjacent areas, possibly the Paleogene complex of Recsk as well. According to this assumption, the main goal of this study is to reconstruct the thermal history (Paleogene burial, Miocene magmatic heating and subsequent exhumation) of Recsk, after its formation. To answer this complex question, we applied the (U-Th)/He thermochronological method, which is sensitive to shallow crustal thermal events (60°C and 180°C for apatite and zircon, respectively), and so, combined

with K/Ar and fluid inclusion data, it is suitable for the reconstruction of the low temperature thermal history of the area. All of the new apatite (U-Th)/He-ages (5.9-19.9 Ma), and most of the zircon (U-Th)/He-ages (17.7-30.7 Ma) are considerably younger, than the Oligocene formation age of the volcanics. Furthermore, there is also a vertical trend in the (U-Th)/He-ages (younger ages with increasing depth). According to these results, the Paleogene rocks must have suffered a thermal overprint, but their cooling postdated the Miocene volcanism, and terminated only in the Late Miocene. In order to determine the most possible time-temperature cooling path, a one-dimensional thermal modelling was carried out, which is also presented in this study.

Exner, P. (1976): *Verh Geol Bundesanstalt Wien*, 2: 3-64.

Földessy, J., Szebényi, G. (2008): *Geosciences, Proceedings of the University of Miskolc Series A, Mining*, 73: 87-101.

## **Groundwater dependent ecosystems in the Duna Valley**

**Viktor Balogh<sup>1</sup>, Szilvia Simon<sup>1</sup>, Marianna Biró<sup>2</sup>**

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Investigation of wetlands and groundwater dependent ecosystems are in the focus of hydrogeological research nowadays. In wetland areas there is a close connection between the vegetation and the groundwater, i.e. the amount of available water and its quality highly specify the type of vegetation. This prevails particularly in saline vegetation.

Our aim was to investigate this relationship by geophysical, hydraulic and hydrogeochemical methods in a study area in the Duna Valley, where two different types of vegetation change sharply: saline meadows and fresh water type marshes.

For geophysical measurement radio magnetotelluric method was applied. With this investigation we can gain information about the resistivity distribution of the subsurface. Since the shallow geological build-up is quite homogenous in the area – mainly consists of sand and pebble – resistivity measurement enables gaining information about the total dissolved solid content of the saturating groundwater. In addition, water level

measurements and chemical measurements were carried out for the characterization of the flow systems in the area.

Comparison between the groundwater chemistry and the vegetation pattern (Biró 2011) unambiguously revealed a close relationship between the vegetation pattern and the groundwater flow systems. The results also highlighted the modifying effect of human interventions on natural flow- and natural vegetational conditions.

Biró M. (2011): Mapping of habitats in Felső-Szűnyogpuszta and historical characterisation of the vegetation and hydrology. Research report for the Kiskunság National Park, Vácrátót, pp. 106

The research was supported by the European Union and the State of Hungary, co-financed by the European Social Fund in the framework of TÁMOP-4.2.4.A/2-11/1-2012-0001 'National Excellence Program' (Simon Szilvia, A2-MZPD-13-0282).

## Construction and analysis of a 3D geological model by using voxelization for the Little Hungarian Plain

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Beside the classical vector models, the voxel based models play an increasing role in geological modeling. The voxel based models are less widespread than vector ones, because of quantitative character, thus are less able to prevail the individual geological knowledge. During the voxelization we define the horizontal and vertical 2D boundaries, then we fill the subsurface space with 3D cubes or any other space-filling bodies, often parallelepipeds (Fig 1.). We also give the value 'void' to any cube that means there are no sufficient or available data for that part of the space.

The aim of the present study is to build a sample 3D geological voxel database from deep boreholes and interpreted seismic profiles.

Voxels are 3D space-filling polyhedrons. In our study, voxels are not cubes, because the resolutions in horizontal and vertical senses are not the same. They are rather flat, tile-like features. Nevertheless, they are equally large, arranged in a rectangular order and they fill the model space completely.

Voxelization is normally used for interpolating numerical values, like density, porosity, resistivity or alike, but in our project we intended to voxelize formation information, that is, rock types and formations described in the boreholes. Since there is no one-software solution yet, we have used a combination of several softwares, creating a processing chain. The used software requires strict stratigraphic sequence of the formations to manage the data. Therefore, we have introduced a somewhat artificial enforced sequence, this way the heteropic facies cannot be taken into account. This is a known problem of our modeling.

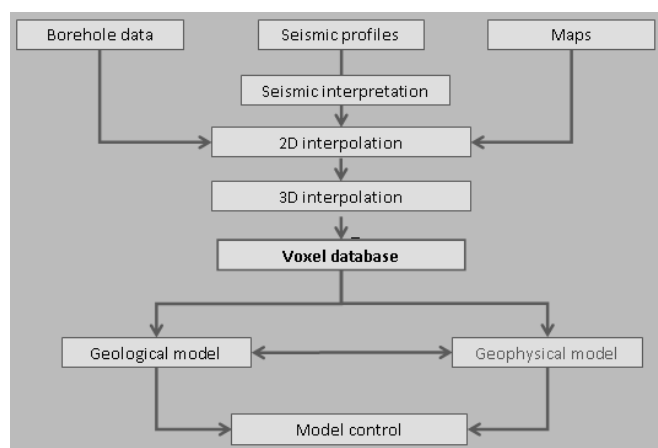


Figure 1.: Flow diagram of the voxelization: These steps are software-independent and in our model they are carried out by different software items indeed

The resolution of the model depends on the sample point density and the thickness of the formation. However the reliability depends on the sampling and types of the interpolation method.

The study area, a 10 km by 25 km rectangular area, is located in the Little Hungarian Plain (NW Hungary), close to Mihályi. In this area Paleozoic rocks form the basement and Miocene, Pleistocene and Holocene sediments fill the basin. The input data of the voxelization were borehole stratigraphic data and interpreted seismic profiles. In its northwestern part we had 6 seismic profiles, while our borehole data are situated along an approximately SW-NE axis. This also means that in the SE corner we do not have any input data: this area selection was intentional. Based on the available data, we got a robust estimate for this area.

We created a  $700 \times 700 \times 10$  m and  $2500 \times 2500 \times 10$  m models with kriging and nearest neighbour interpolation methods (Fig 2.). In the next step we made a quantitative analysis of the voxel models: (1) we calculated some models without some fixed borehole data and compared it with the original dataset then (2) we computed the voxel numbers of each formation in each situation.

The reliability of the voxel models was also examined. The results are in good agreement with the expectation: the reliability of the method decreases with using fewer borehole data. Omitting some crucial boreholes drastically deteriorates the results whereas some other boreholes have less effect on the outcome. Finally the voxel database provides a 3D geological model that can be a help for the 3D geological interpretation.

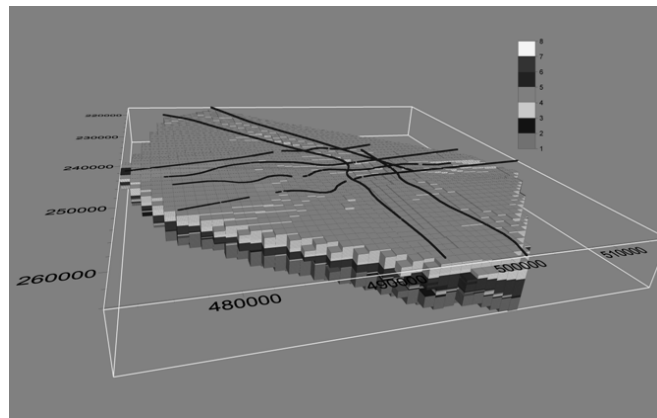


Figure 2.: Voxel model with kriging interpolation. Note that the voxel fill follows the envelope of the input data locations

Our study is a subproject of SourceSink Hungary (NK83400), a project financed by the Hungarian Scientific Research Fund (OTKA), BS partly contributed as an Alexander von Humboldt Research Fellow

## Provenance analysis of the Miocene pebbles of borehole Ib-4 in W-Mecsek Mts., SW Hungary

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The fluvial weathering and transport played the main role in the formation of the Early Miocene conglomerates at the western, northern and eastern edges of the Mecsek Mountains. A statistical and petrological investigation were started to reveal the provenance of the Miocene pebbles and determine the geological settings of the source area.

The Miocene conglomerates create a coherent stripe at the western and northern parts of the Mecsek Mountains, but at the eastern sides of the mountains they occur only in smaller, independent spots. The most of them form the Szászvár Formation, they can be found on the surface and further from the mountains in deeper basins covered with younger sediments as well. The borehole Ib-4 is located close to Ibafa, Western Mecsek. The sequence starts with 11.8 m thick Quaternary clay beds, overlying the Miocene Szászvár Formation. The thickness of the conglomerate is 165.6 m; it is deposited on the Triassic Lapis Limestone.

According to earlier studies (Józsa *et al.*, 2010) the western part of the Szászvár Formation – where the borehole is located – is polymict. The pebbles which were transported from the south are well-rounded; the grain size is often 10-20 cm in diameter. The most common rock types of the gravels are the members of the Upper Carboniferous siliciclastic assemblages (conglomerate-sandstone-aleurite-clay), Permian rhyolite and Mesozoic limestone. There can be found also some “exotic” rocks such as mica schist, gneiss, amphibolite and the very rare eclogite; they occur in the basement of South-Transdanubia. The importance of the white, two-mica granite, contact-metamorphic sandstone and pencil gneiss is outstanding, because these rock types are unknown in the environment of Mecsek Mountains – even in the basement.

A new method was used to specify the geological background of the Szászvár Formation in borehole Ib-4. The precision of determination of the petrology of particular rock types and variability of rock series depends on the size and number of the grains. Although the researchers of earlier studies investigated the rock types microscopically in detail, the number of the investigated

pebbles was too low for statistical treatment. A several times higher amount of individual rock grains would be enough for accurate statistics but the microscopic description of hundreds of singly pebbles would be ineffective. The solution is to choose the smallest possible grain size of the individual rock grains, which provides well visible texture for microscopic rock determination. In most of the cases the appropriate grain size is between 1-2 mm.

There are two types of samples for this research from the Ib-4 borehole: samples with 2-20 cm pebbles appropriate to identify the different rock types, and the 1-2 mm very coarse sand grains for the statistical investigation. The sand fraction was sieved dry and wet. The separated grains were mixed with tile adhesive and filled into a brick shaped form with 4 x 4.5 cm basic area. The completed bricks were used for making 5 x 5 cm thin sections. These preparations contain about 400 grains each. In some depths of the borehole the coarse grained sand fraction was hardly cemented. Such formations have not been considered for further investigations.

During the description of the 2-20 cm pebbles the same types were observed as in the earlier studies, only the amphibolite and the eclogite were not found. The investigation of the small-grain preparations shows that there is a significant rock-type change between the different periods of the Szászvár Formation. However, for the exact determination of the Miocene geological background a correction of possible resedimentation needs to be applied. For this it is necessary to know the petrological composition and possible quantitative proportion of all the older siliciclastic assemblages clasts of which could have resedimented into Miocene sediment. This study can help to reconstruct the regional tectonics and determine the geological settings and unroofing of the eroded area.

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## Flow directions and emplacement mode of a subaqueous ignimbrite based on twofold directional fabric analyses

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Directional fabric – in the sense of preferred grain alignment – of deposits from subaerial pyroclastic density currents (PDCs) are widely reported and are related to forces acting just before the emplacement of the load from the mass flow. In this way, flow direction, source area and emplacement mode have successfully obtained by investigating the flow-related directional fabric (e.g. Giordano *et al.*, 2008) in such cases. On the contrary, the development of fabric in subaqueously deposited volcanogenic mass flows (i.e. subaqueous pyroclastic flows) is not a well-known phenomenon. The implications on flow directions and emplacement mode of a subaqueously deposited ignimbrite are presented in this study, which are based on a twofold petrofabric analyses.

The directional fabrics of the Rám Hill Pumiceous Sandstone were revealed. The formation is known from four outcrops around a deeply eroded Middle Miocene lava dome group in North Hungary, the so-called Keserűs Hill volcano (Karátson *et al.*, 2007). The Rám Hill Pumiceous Sandstone is interpreted as a flow unit of a small ignimbrite that were deposited around the central lava dome group on the proposed ring plain under submarine conditions.

The directional fabric of the present subaqueously emplaced deposit from a PDC-derived mass flow has investigated by a twofold approach: 2D photo-statistical analyses on rock surfaces and anisotropy of magnetic susceptibility (AMS) measurements have also performed. Investigations have made on four outcrops which are scattered on the proposed submarine ring plain.

Anisotropic grain alignment, thus directional fabric have revealed by both methods which indicate well-clustered clast a-axes azimuths and/or imbrication, in this way reliable flow directions. The obtained fabric properties are similar to ones from subaerial PDC deposits, which are reported by many studies (pl.: Capaccioni & Sarocchi, 1996, Giordano *et al.*, 2008). The obtained flow directions along vertical profiles show smaller or greater scatter.

The well-clustered clast a-axes and the imbricated fabrics imply laminar flow motion and high particle concentration (e.g. Rees, 1968) at the stage of emplacement. In this way, in spite of mixing with ambient water and basement sediments, thus dilution during subaqueous movement similar conditions than in subaerial PDCs can be retained under submarine conditions.

The vertical variability of fabric directions (Fig. 1 B) indicates incrementally shifting flow directions during deposition. This observation is in accordance with emplacement by progressive aggradation rather than by freezing 'en masse'.

Considering the obtained flow paths (Fig. 1 A) the investigated flow unit can be originated from the central part of the eroded volcanic terrain, from the Keserűs Hill lava dome group.

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Giordano, G., Porreca, M., Musacchio, P., Mattei, M. (2008): Bull Volcanol, 70: 1221-1236

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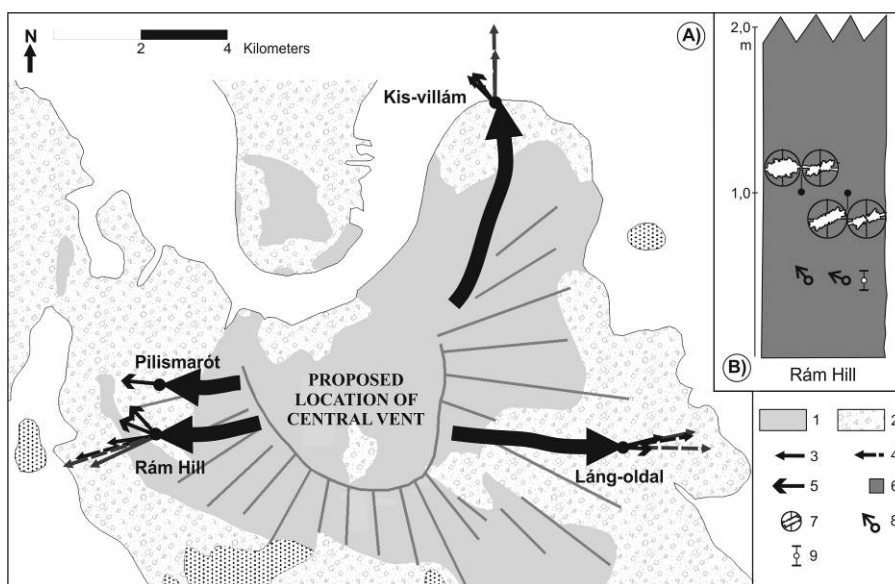


Fig. 1.: Subaqueous flow directions of the Rám Hill Pumiceous Sandstone. A) Inferred flow directions and large scale flow paths, which show a near radial pattern, B) Variation of obtained flow directions along vertical profile at Rám Hill locality; A: 1 - Formations related to core facies, 2 - Formations related to ring plain, 3 - Flow direction from photo-statistics, 4 - Flow direction from photo-statistics are indicated only by the most elongated clasts, 5 - Flow direction from AMS pattern, B: 6 - Investigated flow unit, 7 - Circular frequency of clast a-axes azimuths, 8 - Flow direction from AMS pattern, 9 - Vertical dispersion of AMS samples



## The study and 3D modelling of the Late Badenian basal clastics in the Lobodice subsurface gas storage area

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The Late Badenian clastics in the area of the Lobodice subsurface gas storage belong to the central part of the Carpathian Foredeep and are connected to the Lobodice structure that is an elevation of the pre-Neogene basement. The basement was subject to the Late Badenian transgression. In the transgression sequence, the Late Badenian clastics are succeeded by the sedimentation of the Badenian calcareous clays, which document the deepening of the depositional environment (Brzobohatý & Cicha 1993, Buday 1959, Onderka 1992, Svatuška *et al.*, 1989).

The depositional environment and the provenance of Badenian basal clastics in the area of Lobodice subsurface gas storage was described during the studies of these sediments. The geological model of tectonics and horizons of interest were created as well.

Drill cores of Lobodice wells were described in the total length of 110 m for the purpose of depositional environment description. The textures and structures were described on these cores and on this basis three lithofacies were recognized according to Miall (1996) and Nichols (1999). Well logs were interpreted from sedimentological aspects, 3D seismic measurement was evaluated from aspects of seismic stratigraphy and thus the depositional environment was described. Well log interpretation as well as interpretation of 3D reflexion seismic measurement in total size of 33 km<sup>2</sup> was also done for the purpose of geological modelling. Firstly, the wells and the well tops were converted from depth to time and horizons of interest were recognized. Time conversion was confirmed by synthetic seismograms. The top of Badenian basal clastics and the crystalline basement (the horizons of interest) were picked in the seismic cube as well as fault tectonics. The effect and size of faults were evaluated. The clasts analysis and analysis of the chemistry of garnets and edisonites were done for the purpose of recognition of the provenance of the Badenian basal clastics.

From the results of facies analysis, it was described that lithofacies "A" is a grey, very poorly sorted conglomerate with a matrix supported structure. Results from seismic stratigraphy and well log interpretation show that it is the result of the deposition of a Gilbert-type delta. Reflection terminations on the 3D seismic measurement were described – the upper and lower boundary – and the topsets, clinoforms and bottomsets were recognized on the delta reflections. Lithofacies "B" formed the rippled, fine and medium and very well sorted sandstone, and was interpreted as the result of relatively low energy current probably deposited in marine environment. Lithofacies "C" formed grey, partial lamination, clay siltstone often with bioturbation and was interpreted as the probable result of deposition in the outer part of the shelf influenced by storm activity. From the seismic stratigraphy the coastal onlap was

recognized and the transgression interpreted and connected with lithofacies "C".

It is evident from the interpretation of the horizons of interest, among other things, that the central part of the Lobodice structure is formed by the significant elevation and is terminated by the major normal fault in the north. Despite expectations, the top of basement was distinctly ragged. There are a lot of faults that however crosscut the Badenian sediments exceptionally. It applies for both tops of the horizons of interest that the elevation is bordered by significant depressions in the north and south where the thickness of Badenian basal clastics increases. From a tectonic aspect, the basin was in the extension regime that resulted in domino-effect type faults of grabens and horsts. The faults of grabens and horsts are in the W-E direction and almost do not crosscut marine sediments. Younger faults are mostly in the NW-SE and NE-SW directions.

Petrographic analysis shows the studied Late Badenian clastics are polymictic. Clasts of grey limestone are the most common and often are the largest clasts as well. Clasts of white and yellow limestone, shale and graywacke (most likely Culmian), clasts of quartz and dolomite are also common. Clasts of crystalline rocks make up 9% of the total sample. These results indicate the dominant amount of sedimentary rocks in the source area and recycling of the source material. Petrography interpretation results and garnet analysis results show that the source material was Culmian rock of Drahanská vrchovina and Nízký Jeseník, especially Račice member rocks of the Myslejšovice Formation, rocks of the Protivanov Formation and rocks of the Horní Benešov Formation. The results are confirmed by edisonite analysis as well.

The results will be then used to understand the geological properties of the subsurface gas storage and as the basis for petrophysical and gas flow modelling. The work was conducted in cooperation with RWE Gas Storage, s.r.o. and the software was provided by Schlumberger company.

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## Evaluation of temporal variation of the discharge and physico-chemical parameters of Boltív Spring (Budapest, Hungary)

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Europe's largest thermal karst system is the Buda Thermal Karst, which is situated in Budapest, in the capital of Hungary. The Buda Thermal Karst is a recently active hypogenic karst system (Erőss *et al.*, 2012a). Its discharge area is tectonically controlled and can be found in a narrow zone near the Danube (Fig. 1).

Rózsadomb is one of the three main discharge areas of the Buda Thermal Karst (Fig. 1). In the past, when natural conditions were prevalent in this region, hot (50-65°C) springs with high TDS (800-1350 mg/L) arose close to the Danube and lukewarm (20-29°C) springs with lower TDS (770-980 mg/L) discharged close to the hills. It is supposed that a N-S trending fault zone separate their discharge zones (Erőss *et al.*, 2008). This area is nowadays a fully urbanized environment. The natural springs have been mostly substituted by wells in the last eighty years, only few natural springs are known today, which are drained mostly unused into the Danube.

The lukewarm springs are the results of mixing of two components (Erőss *et al.*, 2012b): a hot one which comes from the deep, regional carbonate aquifer of the Transdanubian Range and a cold one which has a local recharge area in the Buda Hills.

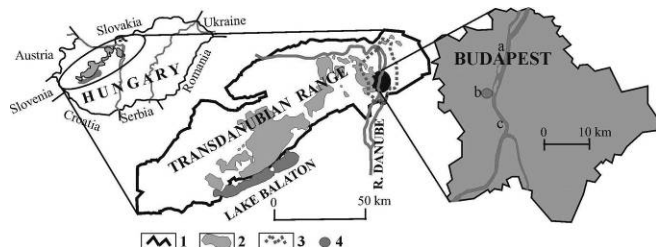


Fig. 1.: Location of the Buda Thermal Karst System in the Transdanubian Range. 1: Subsurface boundary of Mesozoic carbonates, 2: Uncovered Mesozoic carbonates, 3: Buda Thermal Karst System, 4: Boltív Spring, a: Northern discharge area, b: Central discharge area (Rózsadomb), c: Southern discharge area

We studied one of these lukewarm springs of Rózsadomb, the Boltív Spring and Malom Lake which is an artificial lake, fed by this spring (Fig. 2). We studied the changes in the spring discharge and physico-chemical parameters, which may represent the changes of the mixing ratio between the hot and cold components.

We measured discharge, temperature, pH and electric conductivity every four days (from October 2012 to June 2013) in a canal under the Lukács Spa (Fig. 2) where the effluent water of Boltív Spring can be reached. Beside we put a continuous measuring device (Dataqua) into the Malom Lake where the Boltív Spring reaches the lake through an enlarged fracture. Dataqua measured every hour (from October 2012 to July 2013) the level of the lake, the temperature and the electric conductivity. Furthermore we also used archive discharge and temperature data from the 1950-60's in our study.

For every period we compared the variation of parameters to the amount of daily precipitation and water level of the Danube, which

represents the base level of erosion and hence influences the discharge of the natural springs. We made graphs to study the connection between the parameters and for quantitative results we used geomathematical methods. First of all we made descriptive statistics to determine the parameters' variability. In order to analyse the contemporary effect of the precipitation and changes of the water level of the Danube, we used correlation, to determine their delayed effect we used cross correlation.

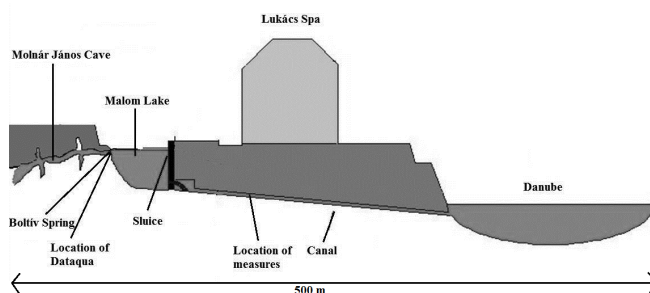


Fig. 2.: Schematic cross section of the study site

As a result from these methods we get that between the parameters and the precipitation the correlation coefficient is low ( $<0.1$ ), which means that there's no linear connection between them. Probably it's due to the large storage capacity of the karst system. Contrary, the correlation coefficient is higher (0.4-0.9) between the parameters and the water level of the Danube. Beside this, the river has a transient effect on the discharge and physico-chemical parameters, which is confirmed by the varying value and sign of the correlation coefficient from time to time. We don't know yet the exact reason for that, and the detailed investigation of this problem is subject of an ongoing research.

With our measures we also strengthen that this nowadays unused spring could be used for geothermal purposes e.g. by heat pump systems. The spring's temperature is stable (20-21.8°C) and the discharge is large enough all year, so it is economical and sustainable resource for geothermal usage.

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# Middle Miocene fossil assemblages and environments in the wider area of Veternica cave (SW Medvednica Mt., NW Croatia)

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In SW Medvednica Mt., near the path to Veternica cave, ca. 16 meters high subvertical outcrop with sedimentary rocks is exposed (Fig. 1). Triassic dolomites in the base are transgressively overlain with dolomitic breccias. Breccias gradually pass into middle-grained breccia-conglomerates, and are later replaced with floatstones containing bivalve moulds and dispersed dolomitic cobbles. Dark grey marl above this layer contains molluscs, solitary corals, bryozoans, echinoids and trace fossils. Within this marly sequence, a layer (biostrome) of more compact calcareous marl with branching sessile colonial organisms (? *Porites* sp.) is clearly distinguishable in the field. Upper part of the column is characterized with light-grey coloured marls with molluscs, containing an intercalation of yellowish sandstones with bivalves and gastropods (Fig. 2). Bivalve fauna is present throughout the grey marls, getting more diverse in upper part of the section. Highest biodiversity occurs within the yellow sandstones, where the first gastropods were found.

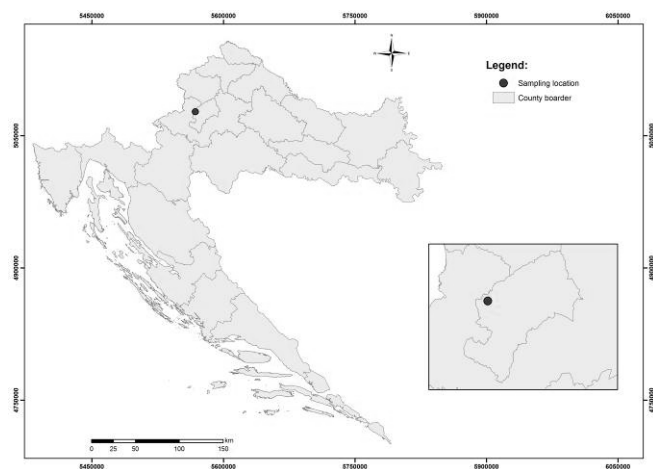


Fig. 1.: Geological setting of the studied area

Determined genera of macrofossils are: gastropods: *Ficus* and *Turritella*; bivalves: *Panope*, *Tellina*, *Lucinoma*, *Corbula*, *Venus* and *Chlamys*; corals: *Flabellum* and ? *Porites*. Additionally, a fragment of irregular echinoid was found. Deeply burrowed Tellinidae are the most abundant molluscs at the exposure, present in a variety of lithologies. Fossils from marls can be determined more easily, because they are preserved with shells. Fossils within yellow sandstones are preserved as casts and moulds.

Marls and sandstones also contain a rich microfossil assemblage: juvenile and fragmented Mollusca, Foraminifer, Ostracoda, Bryozoa, fish teeth and bones, echinoid spines and sponge spicules.

Members of the suborder Rotaliina, Textulariina and Miliolina are recognized among benthic Foraminifers.

According to the fossil assemblage analysis, Middle Miocene (Badenian) age of deposits is determined (Kochansky, 1944; Papp & Schmid, 1985; Studencka, 1986). Sediment succession shows gradual change from shore facies to the deeper inner shelf, reflecting the general transgressive trends in the Central Paratethys, with a short regressive episode and high energy event during the deposition of the yellowish sandstone (Vrsaljko *et al.*, 2006).

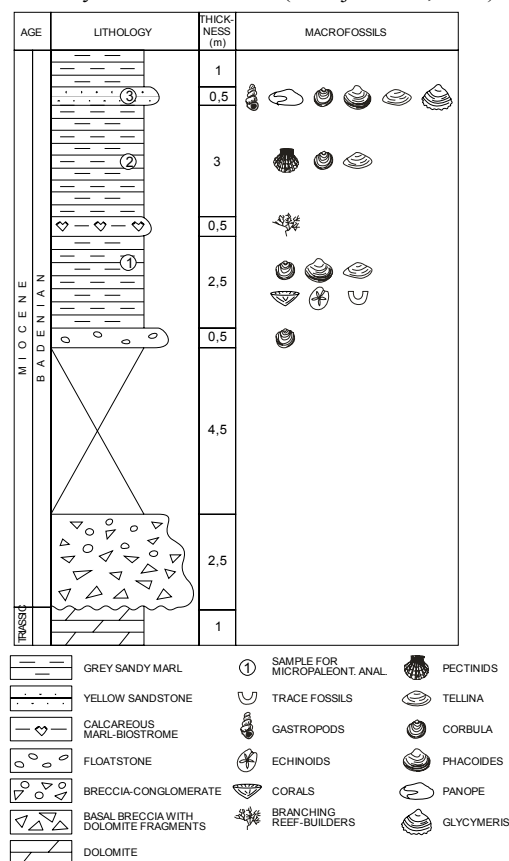


Fig. 2.: Lithostratigraphical column of the investigated outcrop

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## Soricidae and Gliridae fauna of the late Early Pleistocene Somssich Hill 2 locality (South Hungary)

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The Somssich Hill 2 site (Villány Mountains) is situated near the village of Villány. One of the most significant late Early Pleistocene vertebrate fauna of Hungary was turned up from here. The age of the assemblage is approximately 900 ka. The locality was mentioned first by Tivadar Kormos (Kormos 1937) and later by Miklós Kretzoi (Kretzoi 1956) but the most important excavations were made by Dénes Jánossy and György Topál between 1975 and 1984. During the excavations 50 layers (ca. 20-30 cm thickness per layer) were sampled from a ca. 9.5 metres deep, strongly calcified infilling of a karstic fissure. The infilling was loess-like in the upper part of the sequence but became more red and clayey from layer 28. The study of this material is in progress presently at the Department of Palaeontology and Geology of the Hungarian Natural History Museum under the leadership of Piroška Pazonyi. On the basis of the preliminary faunal list of Jánossy (1990) there are several small and large mammal groups present in the fauna.

According to our data, the members of the group Soricidae are represented by 7 species of 3 genera (*Beremendia fissidens* (Petényi), *B. cf. minor* Rzebik-Kowalska, *Crocidura kornfeldi* Kormos, *C. obtusa* Kretzoi, *Sorex margaritodon* Kormos, *S. minutus* Linnaeus and *S. runtonensis* Hinton), whereas out of the Gliridae 4 species of 3 genera are present at the locality (*Dryomimus eliomyoides* Kretzoi, *Glis sackdillingensis* Heller, *G. cf. minor* Kowaski and *Muscardinus cf. dacicus* Kormos). The aim of the present study was the palaeoecological investigation of the locality on the basis of the abundance of the above mentioned small mammal groups in the sequence. The material was predominantly unprocessed, hence first of all the shrew and the dormouse remains were separated from the material. The minimum numbers of individuals (MNI) were calculated for every studied species in each layer, hereby it became possible to follow up the fluctuation of the amount of the shrew and dormouse remains within the sequence.

Shrews provide very important palaeoecological information, since the dominance of the genus *Sorex* indicates colder climate and forested vegetation, contrarily, the members of the genus *Crocidura* are indicators of a warmer climate and more open vegetation. Each of the latter genera turned out from all layers with a high number of individuals. On the basis of the *Sorex/Crocidura* rate at least 5 different types of vegetation were separable at the locality. The lowermost part of the sequence are dominated by *Sorex* shrews, whereas the number of *Crocidura* shrews increases progressively towards the top of the sequence. From layer 35 the *Sorex* species become dominant again, and then a second *Crocidura*-rich phase comes between layer 18 and 12. The uppermost layers show the dominance of the genus *Sorex*.

Large-sized *Beremendia* shrews are also abundant at the locality, exceptionally in layers 32-27 and 15-12. The MNI peaks are in layers 28-27 and layer 13. In the uppermost layers relatively few

specimens were found but layer 5 shows the third and simultaneously the highest record of *Beremendia*.

Although only one extant shrew species is present in the material, the environmental claim of the other species was deducted from the genetically and phenotypically related recent forms. The genus *Beremendia* belongs to an extinct tribe of Soricidae, which has been described from localities with various ecological features. This shrew plausibly was an opportunistic, omnivorous element in the European fauna during the Pliocene and the Pleistocene. The peaks in their minimum and maximum number of individuals correlate with the presence of other hygrophilous groups at the locality (hygrophilous snails and frogs, as well as *Desmana thermalis* Kormos). This suggests that the *Beremendia* could be a hygrophilous form too. Based on the distribution of the hygrophilous groups in the sequence, an open water surface should have been present near the locality in certain periods.

The MNI of dormice has three peaks within the sequence. The first, smaller peak (layers 31-28) is generated by the co-abundance of *Glis sackdillingensis* and *Muscardinus cf. dacicus*. The second maximum, which is the highest (layers 15-11), is caused principally by the enrichment of *G. sackdillingensis* but the other two dormouse species also appear here. The third peak (layers 5-4) is very similar to the latter. Beside the appearance of *M. cf. dacicus* and *D. eliomyoides*, *G. sackdillingensis* is the most frequent here too.

The following paleoecological conclusions were based on the ecological needs of the recent dormouse species, the edible dormouse (*Glis glis* Linnaeus) and the hazel dormouse (*Muscardinus avellanarius* Linnaeus). The *G. glis* prefers principally oak forests with well-developed underbrush, as well as mixed deciduous or riverside forests but old spruce forests too. The hazel dormouse is less specialized and it supremely prefers the bushy parts of the deciduous forests but settles in coniferous woods too, where *Rubus*, *Prunus* and *Corylus* are also present in the underbrush. Moreover, the species has been described from forest steppes and also from *Salix*-dominated shrubby wet areas. The increase of the number of dormice in the sequence overlaps with the rise of the MNI in the case of wood mice (*Apodemus* sp.), *Beremendia* and frogs. This conclusion is in a good agreement with the above described shrew fauna, which suggested, that at least three periods existed, when closed shrubby or forested vegetation was characteristic in the surrounding area of the locality.

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Kretzoi, M. (1956): Geol Hung, Ser Palaeont, 27: 264.

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## Sedimentology of the end-Cretaceous flysch sediments in the SE part of Slovenia

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At the beginning of Mesozoic the territory of the present-day Slovenia was a part of a large uniform carbonate platform. Paleogeographically it was a part of a passive continental margin of Pangea. In the Middle Triassic it broke from the main continental masses due to extensional tectonics caused by opening of the Meliata ocean, creating Apulian tectonic microplate. In its NE part, i.e. in the pre-existing uniform platform area broke in to three paleogeographic units. In the north the Julian Carbonate Platform in the middle the Slovenian Basin, and in the south the Adriatic Carbonate Platform. Adriatic carbonate platform remained relatively stable to the end of Cretaceous when the NE part of Apulian microplate collided with the European continental plate. This formed collision thrust system propagating from NE to SW, with thrust plain oriented NW-SE. In the front of the thrusting, flysch sediments were deposited, thus causing the 'death' of the Adriatic carbonate platform. Studied area is situated in the transitional part between the Outer and Inner Dinarides characterized by lower Mesozoic overlain by deep-water, mostly Cretaceous flysch deposits. It lies in the SE part of Slovenia in the region Bela krajina. Flysch sediments are located in the most eastern part.

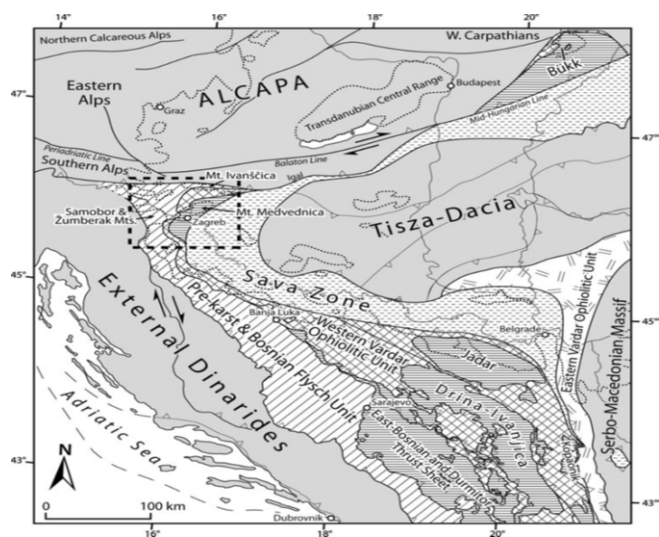


Fig. 1.: Paleogeographical sketch; studied section are situated close the Zumberak Mts. (Lužar-Oberitar, 2012)

Aim of the study was to determine the provenance and age of clasts in limestone breccia megabeds that dominate the basal flysch sediments and also to confirm the age of the flysch sediments. With detailed geological mapping (1:5000) we were able to establish the main geological characteristics of the studied area. Erosional boundary separates the Jurassic limestone from the overlying end-Cretaceous flysch sediments. Flysch sequence is split into the three major parts. The lowest is the basal breccia that was formed with debris flows. The next part is marked by alternating marl and turbidite megabeds. We mapped six megabeds, each of them are at least five meters thick. They were formed with large-scale turbidite flows or based on particular beds also debris flows. Lithology is grading from breccia to coarse-fine grained calcarenite. Third part is

marked with distal flysch deposits. The sampling for microscopical studies has been mostly done along the detailed geological section (1:100). We sampled breccias of the same grain size, from basal breccia and following six megabeds.

The differences in the composition between the basal breccia and megabeds is in the cements and the abundance of clasts but they show no significant differences in composition of lithoclasts. Basal breccia consists of 60 % lithoclasts and bioclasts and 40 % of micritic matrix. Megabeds consist of around 80% lithoclasts and 20% sparitic carbonate cement. Megabeds exhibit upwards also the higher clast-roundness, more clear grading, and overall clearer organisation of turbiditic beds. This indicates the distalisation of the sedimentary environment away from the erosional part of the slope to the more deeper parts of the forming basin.

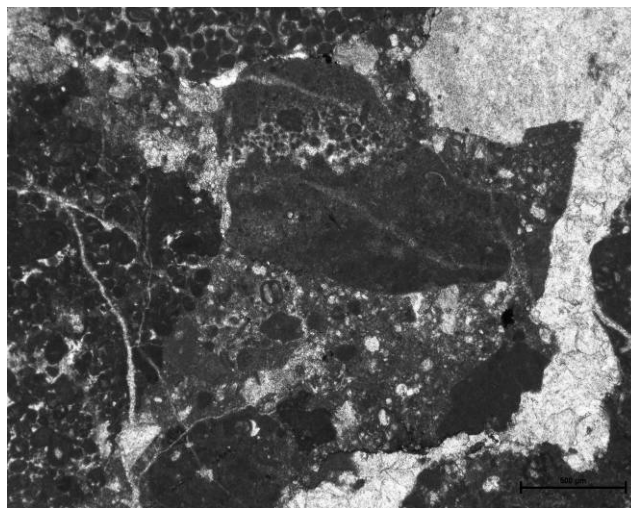


Fig. 2.: Different clasts in turbidite megabed.

With detailed microscopical studies, we were able to distinguish more, than ten different types of lithoclasts. All of them have their provenance from the Adriatic Carbonate Platform. Their age is from Turonian to Maastrichtian. They were deposited in shallow carbonate environments, with different composition depending of the water-energy of the original sedimentary environments. Their composition is changing from micritic clasts with some foraminifers (miliolids) and green algae, to clasts dominated by intraclasts, oolites, foraminifers, brachiopods and the abundance of rudist shells. There are also a lot of bioclasts in the thin sections, mostly consisting of parts of rudist shells. This shows that platform was still active until the upper parts of Cretaceous, more precisely-Maastrichtian stage. Maastrichtian age of the flysch sediments was confirmed by finding of pelagic foraminifera *Globotruncana stuartiformis* Dalbiez in the matrix of the breccia.

Lužar-Oberitar B., Mikes T., Dunkl I., Babič Lj., von Eynatten H., (2012): Swiss J Geosci, DOI 10.1007/s00015-012-0107-3



## Microstructural development of prograde metamorphic sequence from Mt. Papuk (Croatia)

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The metamorphic rocks of the western Mt. Papuk (Slavonian Mts., Croatia) belong to “Progressively Metamorphosed Complex” which grades continuously from low-grade rocks into migmatites and granitoids formed during the Variscan orogeny (Pamić & Lanphere, 1991). With pioneering work of Raffaelli (1964), a complete sequence of index minerals characteristic for Barrovian-type metamorphism was determined.

In this research, geological profile cutting through metamorphic rocks pertaining to characteristic metamorphic zones in the SW Papuk is re-examined and focus is put not only on the index-minerals, but also on prograde mineral assemblages and microtectonical properties of the schists and gneisses.

The southernmost positioned samples, i.e. low-temperature ones, show uniform mineral composition, consisting of Na – plagioclase (albite), quartz, chlorite, muscovite and biotite, representing the schists characteristic for biotite zone of the profile (Fig. 1.).

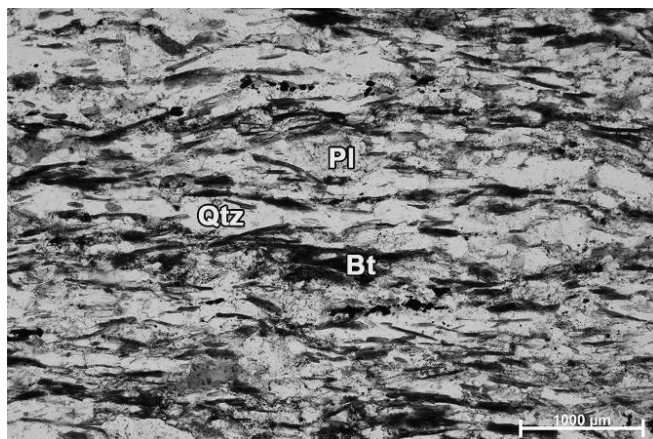


Figure 1. Low-temperature zone of the profile (i.e. biotite zone) of the geological profile cutting through metamorphic rocks, with an accent on mineral assemblage, PPL, N-, Qtz = quartz, Pl = plagioclase, Bt = biotite

The microtextures are characterized by fine-grained spaced schistosity with visible crenulation. Cleavage domains are dominated by muscovite, biotite and chlorite, while microlithons consist of feldspar and quartz, displaying a grain boundary migration as a consequence of dynamic recrystallization.

Toward north the schists grade into the garnet zone, characterized with the appearance of red garnet and the absence of chlorite (Fig. 2.). Recrystallization continued causing the change in the type of foliation from spaced to continuous, while crenulation remained. The increase in temperature is shown as the grain boundary area reduction development in quartz and plagioclase grains.

The zone with highest metamorphic grade determined in this research is the one containing staurolite. The modal composition of gneisses is somewhat changed, therefore no significant amount of muscovite can be found and volume percentage and An content of plagioclase is slightly increasing, as well as volume percentage of quartz.

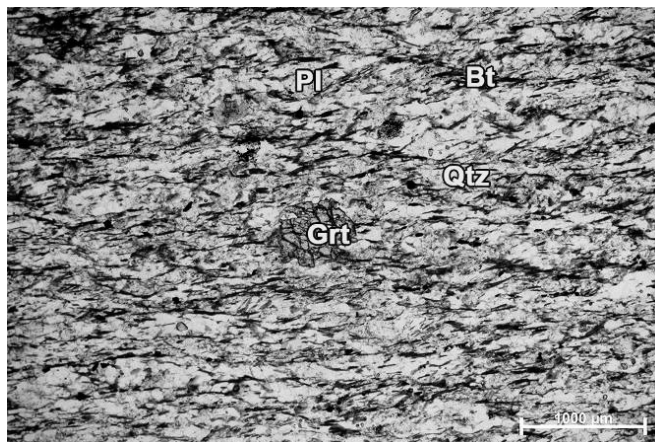


Figure 2. Mineral assemblage of the garnet zone in the researched profile is characterized with occurrence of red garnets, PPL, N-, Grt = garnet

Microtectonically, it is similar to the samples from garnet zone, showing continuous foliation, though in this sample with an absent crenulation and grain boundary area reduction (Fig. 3.). There are two types of opaque minerals visible in all of the samples, represented by hematite and pyrite.

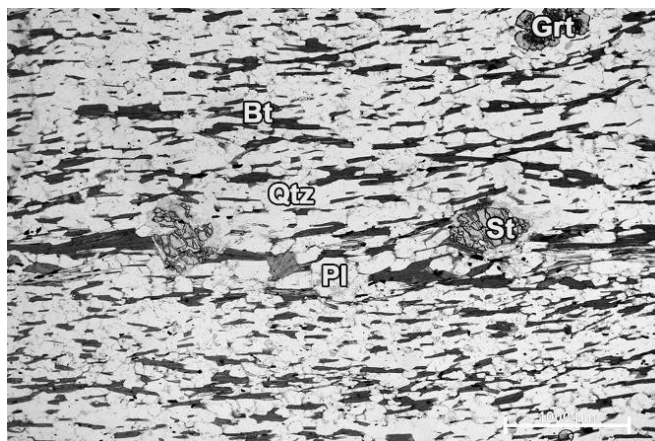


Figure 3. Staurolite zone of the profile developed in gneiss, PPL, N-, St = Staurolite

The investigated samples represent a part of a prograde metamorphic sequence developed in a uniform pelitic protolith, grading from biotite to staurolite zone. Metamorphic zones are regularly distributed from the southern margin to the core of the Mt. Papuk. Observed microtextures follow general prograde character of metamorphism.

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## Hydrogeology of oil and gas deposits of the northern district of West-Siberian artesian basin on the example of the Ugho-Parusovogo field

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The article considers the conditions of ground water formation in the Yuzhno-Parusovoye oil and gas field, located in the Nadym-Pur-Taz district, YaNAO, Tyumen region. The question of the formation of ground waters of oil and gas complex of the Yuzhno-Parusovoye fields is of fundamental importance for the study of hydrogeological conditions of oil fields in the northern areas of the W-Siberian Megabasin. Yuzhno-Parusovii license area is located above the Arctic Circle in the NW-Tazovsky Peninsula. The area is composed of rocks of the Paleozoic folded basement and terrigenous Mesozoic-Cenozoic sedimentary cover (sand and clay). On the territory of the Tazovsky Peninsula, Paleozoic education wells were opened. According to seismic materials, the depth of their roof varies from 6.3 up to 10.0 km. The total thickness of the Paleozoic cover in the area is 1-3 km. The tectonic structure of the Yuzhno-Parusovoye Deposit comprises three structural-tectonic floors: the lower-Paleozoic Foundation, middle-Paleozoic-Triassic riftogenic volcanogenic-sedimentary complex and upper Mesozoic-Cenozoic platform sedimentary cover. Concerning hydrogeology, the Yuzhno-Parusovii license area consists of two water systems, superimposed on each other: the Mesozoic-Cenozoic and the Riphean-Paleozoic. Thus only the upper part of the Mesozoic-Cenozoic water system is studied, which will coincide with the sedimentary cover and consists of two hydrogeological levels.

Data on the hydrodynamic characteristics of the field are difficult to interpret; therefore a special attention is paid to the aquifers of the Yuzhno-Parusovoye field. On this territory, there are pre-requisites for the formation of the inverse hydrochemical zonality.

Normal vertical hydrochemical zoning of groundwater is manifested through a cross section of the earth's crust and is expressed in a regular change of hydrodynamic and hydrochemical parameters. It is an obvious change of genetic types of water of  $\text{HCO}_3\text{-Ca-SO}_4\text{-Na}$  through the  $\text{Cl-Mg}$ ,  $\text{Cl-Ca}$  from areas of the external power supply to the Central most omitted parts of the basin. Along with the normal, in many artesian basins, especially in the oil and gas bearing structures, the presence of the hydrochemical inversion is noted. Inversion of vertical hydrochemical zonality, which are characterized by well marked reduction of mineralization of groundwater the depth of the aquifer and corresponding changes in their chemical composition, are currently for hydrogeological areas of different types.

Types of inversion cuts original unit in three groups. Group with a local increase in the salinity in the upper parts of the section, preserving ancient infiltration water and education «revived» fresh waters of the recrystallization clays, introduction of deep fresh water from the more high temperature zones of the sedimentary cover or from the basement. Special attention will be paid to the last two types of inversions. Proceeding from the aims of the work, the lower hydrogeological level, which is associated with the major hydrocarbon fields is discussed.

Test results show salinity decrease from 18 g/l up to 6 g/l on average in the upper Cretaceous during the transition to lower Cretaceous. In addition, there is a change of water type from  $\text{Cl-Ca}$

to  $\text{HCO}_3\text{-Na}$ . It should also be noted that the absolute and relative content of  $\text{HCO}_3$  ions in the waters increased from 4.3 to 23.7 variance%. Simultaneously with the increased content of  $\text{HCO}_3$  ions micro component composition is changed, which manifests itself in increasing B/Br ratio with depth. To determine the Genesis of the deep waters of Yuzhno-Parusovoye fields B/Br ratio was used. Increase of B/Br ratio points to the inflow of high-temperature water into the reservoir. Both of these elements are present in oceanic waters, in fairly constant amounts average content of Br is about 65 mg/l, the average content of B varies in the range of 5 to 12 mg/l. However, the conditions of accumulation of these elements in the ground waters differ significantly.

Thus, if we take the average value of the B/Br ratio for oceanic water (0.08-0.18) the sharp increase will testify the receipt of B with high-temperature deep fluids. B/Br ratio varies from 0.95 to 3.9. With depth an increase is observed in the B/Br ratio. Increase of B/Br ratio can be connected to two reasons: 1) removal of argillaceous rocks high temperature water ( $T>100$ ); 2) the process of evaporation-condensation. To confirm this hypothesis calculations by Bychkov and Kireeva, which was thermodynamic modelling, has resulted in a graph, which is easy to diagnose the presence of condensation water, both anthropogenic and natural origin.

Based on the data of chemical analyses from the Yuzhno-Parusovaya square a graph was constructed to illustrate the dependence of B/Br coefficient on water mineralization. The similarity of the graphs obtained by simulation and by results of chemical analyses, gives us the right to assume the same mechanism of formation of technogenic condensate waters and stratal waters Yuzhno-Parusovoye oil field. In both cases, the chemical composition of water formed as a result of mixing of deep condensate connate waters. The graph shows significant increase in B/Br ratio with decreasing water mineralization.

B/Br relationship gives us the right to say about the transfer of boron with low mineralized waters. This low mineralized water must be very high temperature, because with a temperature increase is associated sharp increase in the relative content of B in water. If reduction of mineralization of the studied water was associated with dilution by infiltration waters, B/Br ratio remained constant, as in seepage waters B and Br present in trace quantities. Thus dramatically increasing in this case B/Br attitude apparently reflects the inflow into the reservoir connate water endogenous deep waters. Increase of B/Br ratio indicates the removal of argillaceous rocks in the high temperature waters and the process of evaporation-condensation. Education fresh formation water is  $\text{HCO}_3\text{-Na}$  Yuzhno-Parusovoye fields (inversion) occurred with the introduction of connate water reservoir of high-temperature gas-steam deep fluids. This is proved by the sharp rise In/VG relations than the values for sea water and sedimentation brines. This increase is due to: 1) condensing vapour and condensate enriched B, compared with the initial solution; 2) B removal of argillaceous rocks of high-temperature waters.

## Effects of exhumation in the hydrocarbon exploration of the Snøhvit Field, Hammerfest Basin, Norwegian Barents Sea.

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The Barents Sea is well known for its unusual basin evolution and complex uplift history which have resulted in the discovery of abundant gas and little oil. Several recent oil and gas discoveries in the southwestern Barents Sea are now triggering an increased interest in this huge, largely unexplored petroleum province. The complexities of the Hammerfest Basin necessitate the use of all available geological and geophysical information when undertaking regional interpretations, play fairway assessments and prospect definition. In order to study the petroleum system, it is also important to investigate exhumation effect on the rock properties and hydrocarbon prospectivity. This study focuses on estimation of Cenozoic exhumation in the Snøhvit field that comprises three discoveries; Snøhvit, Albatross and Askeladd (Fig. 1).

An integrated approach, using well log data and published compaction curves (Mondol *et al.*, 2007, Mondol 2009), has been utilized to estimate Cenozoic exhumation. This estimation is based on transition zone between mechanical and chemical compactions. Bottom hole temperature has been used to infer the transition zone temperature. On the basis of transition zone, the estimation for exhumation is investigated. A suite of well logs from 15 exploration wells from the Snøhvit area, has been taken into account. The transition zone from mechanical to chemical compaction marked on the basis of grain framework stiffening due to the onset of quartz cementation as long as the surface area is available for precipitation of quartz and temperature is higher than 70°C.

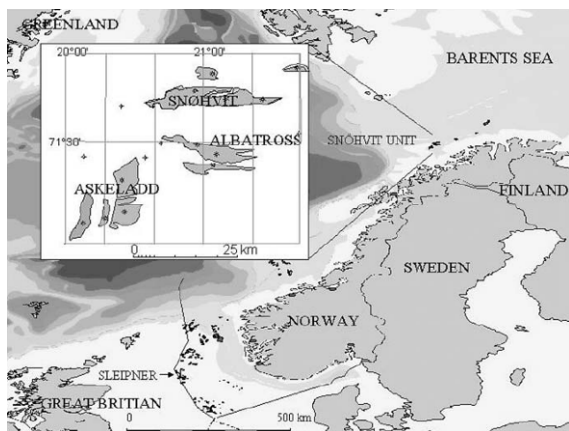


Fig. 1.: The map showing the location of Snøhvit area (after Maldal & Tappel, 2004).

Compaction of sediments occurs due to effective vertical stress at a shallow depth (mechanical compaction) and dissolution of unstable minerals and precipitation of new and more stable minerals at a higher temperature corresponds to greater burial depth (chemical compaction). Due to the combine effect of mechanical and chemical compaction, the rock properties such as velocity, density and porosity alter continuously with increasing burial depth (Mondol *et al.*, 2007).

Our analyses show that the present day transition zone temperature in the study area does not match with the actual temperature reflecting the Hammerfest Basin as an exhumed basin. The compaction trends, particularly, velocity versus depth found in the studied wells have been used to investigate the transition from mechanical to chemical compaction. When sonic velocity versus depth trends have been compared with published compaction curves, there was found a mismatch on the basis of which exhumation was calculated. The calculated exhumation estimates differs for Snøhvit, Albatross and Askeladd discoveries depending upon the structural configuration (Fig. 2). The exhumation for Snøhvit discovery is from 300 to 800 m increasing from west to east whereas, in the Albatross discovery it increases in opposite direction ranging from 700 to 1000 m. In the Askeladd discovery it ranges from 300 to 1000 m and decreasing from south to north. This exhumation estimation is in accordance with the published literature (Ohm *et al.*, 2008, Henriksen, 2011).

It is clear from our investigation that a complex burial history of the Hammerfest Basin involving uplift, erosion and renewed burial during Cenozoic time has influenced the distribution of oil and gas in the reservoirs and the position of fluid contacts.

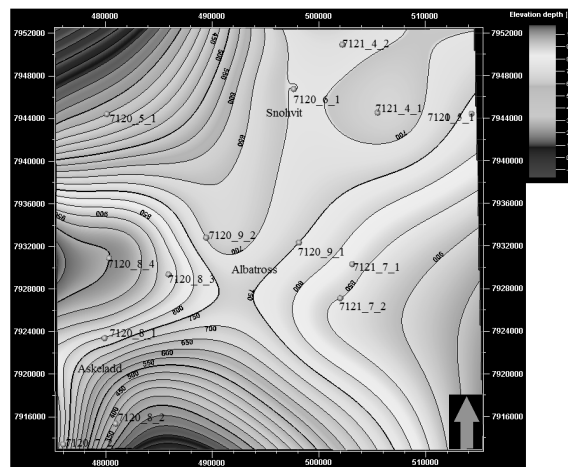


Fig. 2.: Contour map (Butt, 2012) showing exhumation based on the experimental curve (Mondol, 2009) kaolinite-silt (50:50) in the Snøhvit development.

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# Compaction and rock properties development of Mesozoic and Cenozoic mudstones in the Hammerfest Basin, Norwegian Barents Sea.

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This study focuses on compaction and rock properties development of Mesozoic and Cenozoic mudstones in the Hammerfest Basin, Norwegian Barents Sea (Fig. 1). The area is highly faulted due to tectonics resulted several stages of uplift and erosion. An integrated approach, using a suite of well log data from 6 exploration wells and published mudstone compaction curves (Mondol *et al.*, 2007, Mondol, 2009), has been utilized to understand the shale rock properties as a function of burial depth under the effect of both mechanical and chemical compaction. For shale volume calculation, a cutoff of  $V_{sh} \geq 0.75$  has been applied for shale data points in the gamma ray log of all the studied wells. Bottom hole temperature has been used to infer the transition zone temperature.

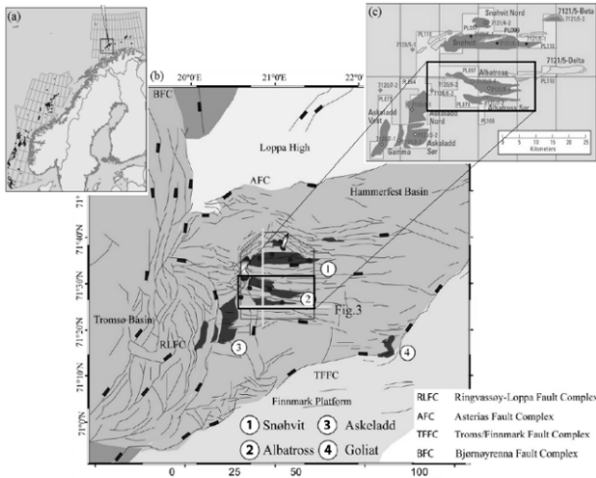


Fig. 1: (a) Location of the study area, highlighted with black rectangle (Modified from Wennberg *et al.*, 2008) (b) structural elements of the Hammerfest Basin (Modified from Ostanin *et al.*, 2012), (c) location of the wells used (Modified from World oil).

Vp-depth and density-depth crossplots of Mesozoic and Cenozoic mudstones of six studied wells show that the present day transition zone depth from mechanical to chemical compaction occur in the Knurr Formation of the study area which is obviously marked on the basis of sharp increase in the velocity versus depth trends (Fig. 2). All the formations younger than the Knurr Formation are dominated by mudstones. Due to the combine effect of mechanical and chemical compaction, the rock properties such as velocity, density and porosity alter continuously with increasing burial depth (Mondol *et al.*, 2007). Gamma ray log does not show much variation within Knurr Formation in the study area. This indicates a uniform lithology distribution throughout study area. Thus, onset of quartz cementation as a function of temperature is accountable for the increase in velocity. The present day complex structural configuration of the Hammerfest basin described the variation in the transition zone depth from well to well. Moreover, temperature plays a vital role in changing the compaction processes from mechanical to chemical compaction. Lower velocities in the overpressured rocks have been related to the reduction in the effective vertical stress that

results in less mechanical compaction and preservation of the primary porosity. Present day temperature of the transition zone in the Snøhvit development is not sufficient to start a transition from mechanical to chemical compaction. It is lower than the standard temperature (70-80°C), giving indication of exhumation (Fig. 3).

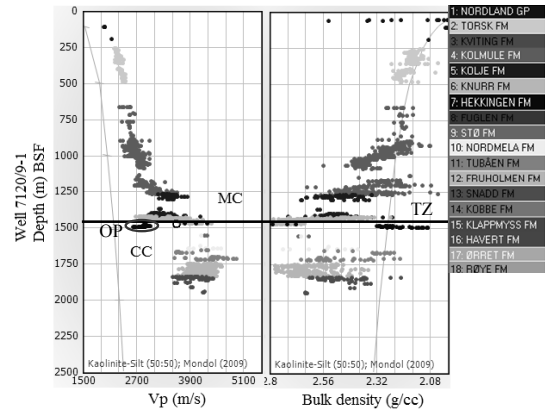


Fig. 2: The velocity, density versus depth cross-plot showing the demarcation of transition zone from mechanical (MC) to chemical compaction (CC). Red circle is showing over-pressured zone.

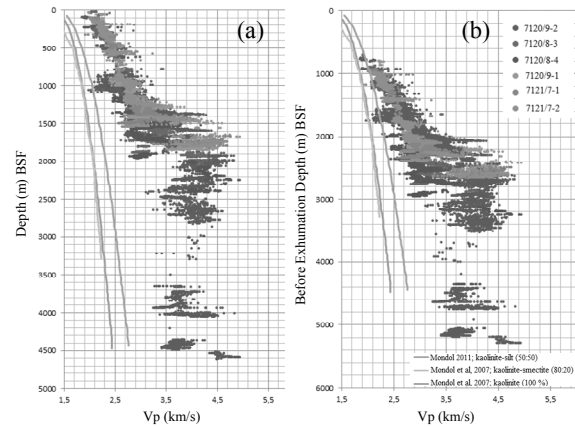


Fig 3: Velocity-depth crossplot of shale data points in all the studied wells (a) before and (b) after exhumation correction.

It can be stated from our study that the rate of sedimentation, mineralogical, textural and temperature variations with depth and time, overpressure, exhumation and types of pore fluid in the sediments are the factors should be taken into account while investigating compaction and evolution of rock properties.

Mondol, N. H., Bjørlykke, K., Jahren, J., Hoeg K. (2007): Marine Petrol Geol, 24: 289-311.

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## Sediments from the karstic lake Visovac (Krka River, Croatia)

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Sediments from the karstic lake Visovac (Krka River, Croatia) were investigated to evaluate metal input and temporal and spatial environmental changes. Sediment was sampled at three locations (VT, VL, VS) (Fig. 1) using a hand driven acrylic corer by scuba diver where undisturbed sediment and continuous sedimentation were expected. In total 14 sediment cores (15 cm) were analysed for sediment content of major (Ca, K, Fe, Mg, Ti, Al) and minor (Pb, Cu, Zn, Rb, Sr, Zr, Ba) elements, activities of natural radionuclides ( $^{40}\text{K}$  and  $^{232}\text{Th}$ ), stable isotope compositions of organic carbon and nitrogen ( $\delta^{13}\text{C}_{\text{org}}$  and  $\delta^{15}\text{N}$ ), as well as stable isotope composition of sedimentary carbonate ( $\delta^{13}\text{C}_{\text{carb}}$  and  $\delta^{18}\text{O}_{\text{carb}}$ ).

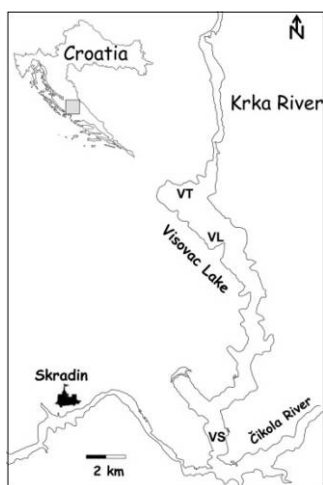


Fig. 1.: Visovac Lake with sampling locations.

Correlation coefficient method was used to assess the interrelations between the investigated elements that could indicate the existence of the same source or behavior for two or more elements. Correlation was made between the normalized element concentrations. The Al was used as conservative parameter. Only correlations with  $p < 0.05$  or better, that simultaneously have c.c.  $> 0.7$  are taken into account. Strong positive correlations were found between the contents of Al, Fe, K, Zr, Rb and Ti. The Al, Fe, K and Ti are typical terrigenous elements, so dependencies between these elements can be explained by their common natural source, most probably originating from erosion of bauxite deposits and terra rossa, which are present in this area (Miko *et al.*, 1999). Very strong dependencies were also found between the sediment content of Ca and Sr (c.c. = 0.99), Ca and Ba (c.c. = 0.96), Ba and Sr (c.c. = 0.96). Strong positive correlations between these elements indicate their common association with carbonates. The Zn and Mg show no significant correlation with the

rest of analysed elements. Such behavior of Zn is probably consequence of its anthropogenic origin. Regarding, sediment quality guidelines (SQG) for freshwater ecosystems (MacDonald *et al.*, 2000) Zn is only analysed element whose concentrations (10-15 cm, upper part of the Lake) where above TEC value. The Pb and Cu were below the detection limit.

Observation of spatial and temporal variation of typical terrigenous elements (Al, K, Fe, Ti) showed that much higher values can be found in the upper part then in the lower part of the Lake. This indicates that majority of terrigenous material was deposited in the upper part of the Lake Visovac. Observed decrease of values with depth indicates decrease of terrigenous material input over time. These temporal and spatial changes were conferred by activities of natural radionuclides.

Variations in carbonate C and O stable isotope composition are a result of a combination of changes in abundance of particulate and dissolved C sources, through biogeochemical processes and erosion (Herczeg *et al.*, 2001). The obtained  $\delta^{13}\text{C}_{\text{carb}}$  and  $\delta^{18}\text{O}_{\text{carb}}$  values at all investigated sites are typical for authigenic lacustrine environments (Cukrov *et al.*, 2013). This indicates that the primary source of carbonate in the sediment is the in-situ precipitation from the river water constantly supersaturated with respect to calcite (Lojen *et al.*, 2004). Obtained  $\delta^{15}\text{N}$  values are found in narrow range (between 5.4‰ and 7.9‰) and increasing with depth.  $\delta^{15}\text{N}$  values in general resemble the values observed in lakes with predominant autochthonous primary production (Vreća & Muri, 2006). Obtained  $\delta^{13}\text{C}_{\text{org}}$  values are found in wide range (between -34.77‰ and -29.39‰) and increasing with depth. Large differences between surface layer and 10-15 cm layer indicate a gradual change in SOM sources and diagenetic processes – decomposition of SOM that modified its carbon stable isotope composition (Cukrov *et al.*, 2013).

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# Lithological detachment surfaces in a German potash mine – an interdisciplinary approach to minimize a longtime safety issue

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The detailed knowledge on the geological characteristics and geochemical behaviour of evaporitic rocks is crucial for the safety in potash mining. Evaporitic rocks (e.g. rock salt, sylvinite) are frequently interbedded with thin layers of clay or anhydrite, which are known as detachment surfaces (“Löserflächen”). Those detachment surfaces are attributed as safety issues for decades in the underground potash mining. Due to the convergence of the overburden rocks and the decompression in excavated mine openings, detachment surfaces are preferred zones of structural weakness at the roof of potash mines. The expansion of the present-day mines to greater depths with a higher thickness of overburden rocks demands a revision and re-evaluation of the geological knowledge of detachment surfaces.

My study is based on descriptions and field data from the evaporitic Zechstein basin (Upper Permian) in Central Germany according to Reichenbach (1970). The Central German Zechstein Basin is composed of cyclically deposited saliniferous rocks (limestone – anhydrite – rock salt – sylvinite – claystone) with a normal thickness of about 400 m, followed by Triassic sand- and limestones with a thickness up to 1000 m.

I will focus on detailed stratigraphic, mineralogical and geochemical investigations of the rock salt interval in the Leine evaporitic cycle (Zechstein, Upper Permian). The so-called “Hangendes Begleitsalz” has been deposited subsequent to commercially excavated potash seam “Ronnenberg” with an average thickness of about 10 m (Fig.1). The formation of the “Hangendes Begleitsalz” consists of coarse crystalline halite, interbedded with continuous layers or flaky aggregates of microcrystalline anhydrite. The thickness of the single halite beds is 10 cm to 40 cm with an overall colourless to light grey, sometimes brownish-orange appearance in the upper or lower parts (Reichenbach, 1970). A few anhydrite beds also contain polyhalite, clay and talc. Previous studies have shown that those mixed anhydrite beds are preferred zones of structural weakness. However sufficient knowledge of the geology of detachment surfaces has not been gained so far.

Thus, detailed geoscientific investigations of detachment surfaces will help to increase the safety in mining. The methodical background of my studies includes underground mapping of the “Hangendes Begleitsalz” halite formation linked with close meshed sampling of the detachment surfaces. Mineralogical, geochemical

and thin section analyses, supported by scanning electron micrograph (SEM) data will help to determine the quantitative and qualitative mineral content of the samples. The traceability of the detachment surfaces throughout the mining claim will be proven by the re-interpretation and analysis of surface- and underground drilling data as well as underground mapping data.

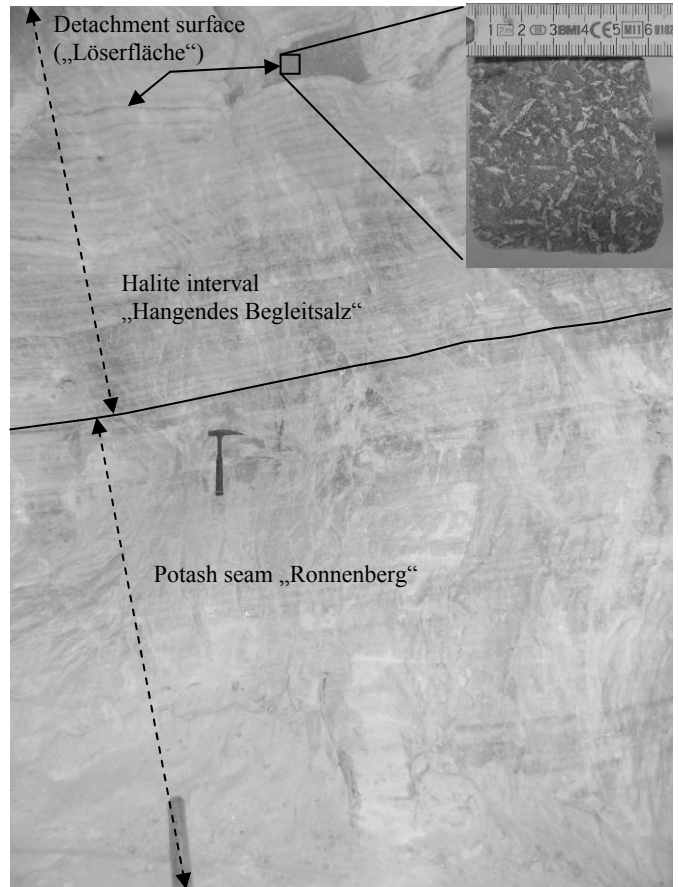


Fig. 1: Potash seam “Ronnenberg” and halite interval “Hangendes Begleitsalz” with detachment surface (“Löserfläche”) (Dabrowski, 2013)

Reichenbach, W. (1970): Der Zechstein auf der Scholle von Calvörde – TU Bergakademie Freiberg, 200 p.

## Biostratigraphy and paleoecology of the Upper Cretaceous – Lower Paleogene deposits of the Skole Unit of the Polish Outer Carpathians based on foraminiferal assemblages

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The studied area is located in Polish Outer Carpathians in the most external major unit of them, called Skole Unit. The basic studies are carried out in the field of the western part of the Przemyskie Foothills between localities of Dynów – Krzywczyna – Bircza – Temeszow (Fig 1). This unit is composed of Lower Cretaceous to Lower Miocene deep-sea sediments accumulated in the Skole Basin, next folded and thrust northward during the Miocene.

In many places around the world the Cretaceous – Paleogene boundary has been accurately determined on micropaleontological analyses based mainly on occurrence of planktonic and benthic foraminifers as well as calcareous nannoplankton, ostracods, dinoflagellates, pollen and plants disputes in deep-sea sediments. Also, the Cr/Pg boundary studies are carried out in deep-sea sediments of two regions of the Polish Carpathians. The first one is located near Rzeszow and the second one near Dynów (Fig. 1). Both will provide one comparative summary.

Studies were focused on interval which could contain the Cretaceous - Paleogene boundary. These are sediments of Ropianka Formation in older literature known as Inoceranian Beds. Ropianka Formation is composed of “flysch” (turbidite) deposits which include sandstones, mudstones and thick layers of grey and grey-bluish marls, etc. For foraminiferal studies the most valuable are the hemipelagic and pelagic deposits which contain the most autochthonous, rich, well-preserved planktonic and benthic foraminiferal assemblages. These assemblages allow to determine the age of this boundary to the biostratigraphic biozones resolution and to estimate depositional environment, basin paleobathymetry as well as to observe microfaunistic changes before and after the latest Maastrichtian extinction.

Samples were subjected to mechanical disintegration in the sludging laboratory at the Institute of Geological Sciences at the Jagiellonian University in Krakow using Glauber's salt (sodium sulfate) and liquid nitrogen. Rock disintegration with liquid nitrogen is a new method (Remin *et al.*, 2012) which gains increasing popularity in micropaleontological laboratories. It allows reducing the disintegration time up to two hours and leave less residue. The old method by using Glauber's salt could took up to 1-

2 months to its full disintegration (it depends on the type of rock and strength of cementation).

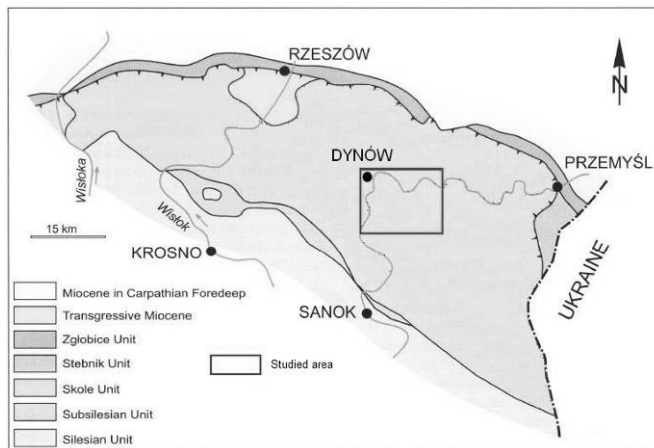


Fig.1.: The studied area of the Skole Unit in the Polish Carpathians (after Zytka *et al.*, 1989; Rajchel 1990; Barwicz-Piskorz & Rajchel, 2012, modified)

On the basis of a very well-preserved and diversified planktonic and benthic foraminifer species the interval of the Maastrichtian - Paleocene boundary occurrence has been narrowed down in Rzeszow region to 40 centimeters (Gasiński & Uchman; 2009, 2011). Therefore, the Dynów region has been selected to recognize such boundary event, hoping to establish in the studied sections more narrow and precise the Cretaceous/ Paleogene boundary.

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Gasinski, M.A., Uchman, A. (2009): Geol Carpath, 60/4: 283-294.

Gasinski, M.A., Uchman, A. (2011): Geol Carpath, 62/4: 333-343.

Remin, Z., Dubicka, Z., Kozłowska, A., Kuchta, B. (2012): Marine Micropaleont, 86-87: 11-14.

Special gratitude for Polish Geological Society and Jagiellonian University Doctoral Society for granting this project.

## Basin analysis of potentially gas-bearing Lower Carboniferous shales in the area of Fore-Sudetic Monocline

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Moravo-Silesian Basin belongs to foreland basins system of the Varican orogeny. Northern section of Moravo-Silesian Basin comprises Lower Carboniferous sediments which were analysed as potentially hydrocarbons bearing rocks.

The data used in the research had been collected during sedimentological profiling of five archival cores. Sediments of western part of investigated area were described as proximal flysch facies comprising sandstones, mudstones and some conglomerates. East-trending facies distalization was observed. Distal facies are represented by black shales intercalated with very fine-grained sandstones. In the south-eastern direction a transition of flysch facies into carbonate facies was observed.

The analysed sediments are arcose wackes, arcose-lithic wackes, silty mudstones and mudstones. Increasing mineral maturity in Lower Carboniferous sediments was discovered what is demonstrated by decreasing content of lithoclasts and increasing content of quartz and feldspar grains towards the top of the succession.

Lower Carboniferous flysch sediments are very organic-matter and pyrite rich. Scanning electron microscope analysis also revealed the presence of bastnaesite what is the evidence that the rocks have not undergone high-temperature processes.

The values of TOC range from 0.7 to 1.65% and are sufficient for hydrocarbon generation. According to data from the southern edge of the study area vitrinite reflectance values reaches 2.26-4.59% (dry gas window to overmature stage). The organic matter of Lower Carboniferous flysch sediments contains gas-prone, type-III kerogen.

Optimal conditions for forming of unconventional hydrocarbons (shale gas) were stated in the area located between the Kraków-Lubliniec (Hamburg) fault zone (northern boundary) and parallel of latitude of Kędzierzyn-Koźle (southern boundary).

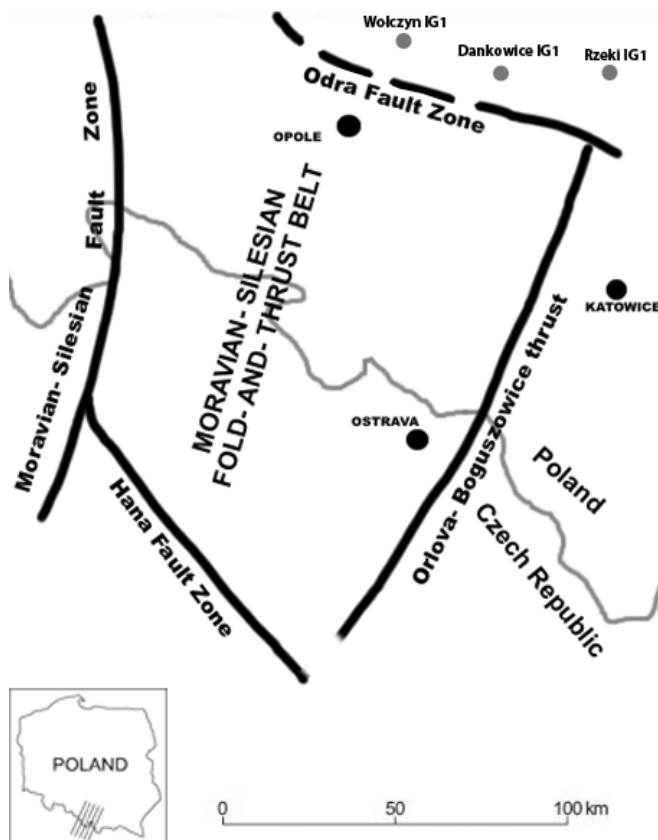


Fig. 1.: Structural elements of the Moravo-Silesian Basin (modified after Buła *et al.*, 2008).

Buła, Z., Żaba, J., Habryn, R. (2008): Przegląd Geologiczny, 56: 912-920

## Influence of secondary changes on the physical and mechanical properties of volcanic rocks in Yagodninskoe zeolite deposit in Kamchatka Peninsula

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Yagodninskoe deposit is a large deposit of natural zeolite which has been prospected in Kamchatka Peninsula. It is confined to the extrusive-subvolcanic complex of the Miocene-Pleistocene age and belongs to the same named ore-forming hydrothermal-magmatic system.

The studied zeolite-bearing productive stratum was formed under intense heating of perlites and tuffs dacitic and liparitic composition in the upper part of the hydrothermal system.

The main target of presented research is to study alterations of volcanic rocks, to identify types and morphology of zeolites, to determine petrophysical properties of host rocks and to assess the effect of hydrothermal alteration on rock properties.

The host rocks are mostly lapilli, or rarely coarse ash tuffs, consisting of a combination of crystal, rock and glass fragments cemented with vitric matrix. Under the action of thermal water tuffs change their composition, pore-space morphology and volume, and properties, finally transforming into zeolitic or argillic-zeolitic rocks. The original mineral assemblages of volcanic rocks are dissolved and replaced by secondary minerals among which zeolites (clinoptilolite, mordenite, heulandite) are the most abundant; silica oxides, smectites, chlorite, and calcite also occur (figs. 1, 2). Volcanic glass are the most sensitive to alteration totally replaced by zeolites; pyroxene and plagioclase are more stable, while magmatic albite and quartz are the most stable. The intensity of alteration changes from medium to almost 90-95% altered rocks. By the degree of secondary transformation rocks are divided into three groups: almost altered (amount of secondary minerals to 95%, zeolite content up to 90-95%), highly altered (amount of secondary minerals to 85%, zeolite content of about 80%) and average change (amount of secondary minerals to 60%, zeolites - up to 35%). Zeolites substitute volcanic glass, fill pores and fractures, and occur as filmy cement.

Several generations of zeolites, differing in crystal size, morphology and composition were revealed. In general, tuffs are characterized by high porosity but low permeability; they are weak or moderately weak and are resistant to water saturation. The highly argillized tuffs are the weakest and unstable in water-saturated state. It was found that strength and elastic modulus decrease along with increasing porosity and intensity of alteration.

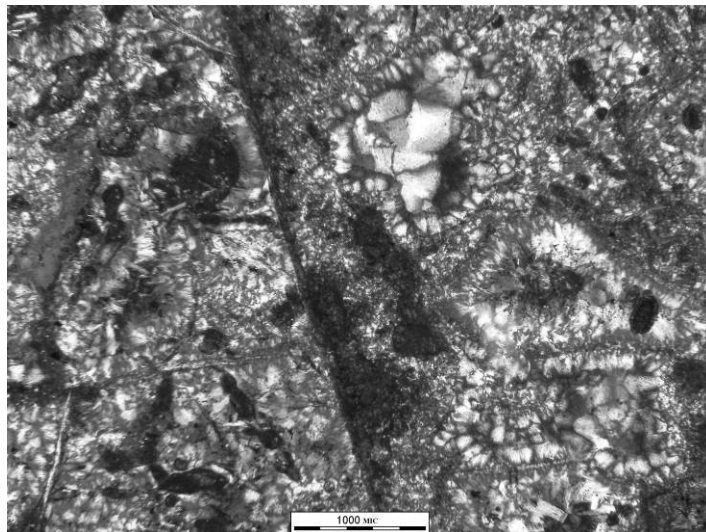


Fig. 1.: Alteration of vitroclasts in almost altered tuff by zeolite and smectite (photo of microsection +N).

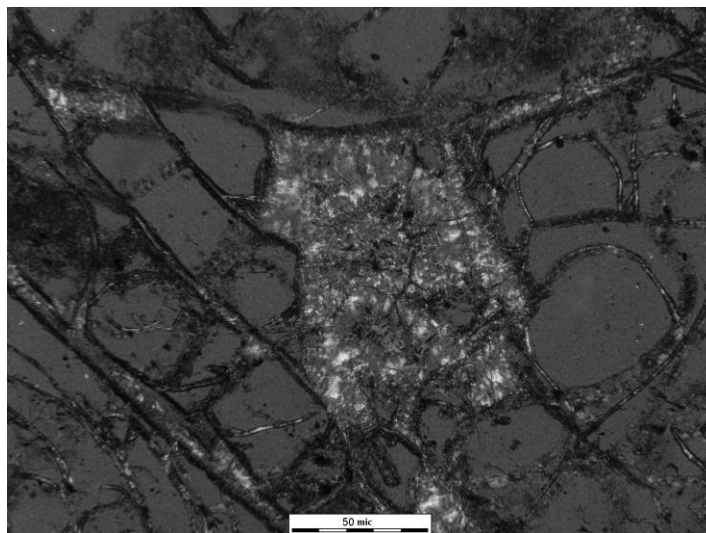


Fig. 2.: Alteration of perlite fill pores and fractures by zeolite (photo of microsection +N).

## Petrographical and geochemical study of the magmatic phases and hydrothermal vein types of the Bolcana porphyry Cu-Au mineralization

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The Bolcana porphyry Cu-Au mineralization is located in the southern part of the Apuseni Mountains (Romania), where Miocene calc-alkaline intrusive and volcanic units host numerous porphyry Cu-Au and epithermal Au-Ag (Pb-Zn) mineralizations (Neubauer *et al.*, 2005). The Bolcana ore deposit is located in the central part of the Bolcana-Troița-Magura volcanic structure and is hosted by the Neogene Hondol-Faerag Andesite and the Bolcana Intrusive Body. The porphyry copper mineralization is represented by chalcopryite, pyrite, bornite, magnetite, hematite, molibdenite and subordinate native gold ore minerals. This mineral assemblage is associated with potassic, sericitic, sericite-chlorite, propylitic and intermediate argillic hydrothermal alterations. The porphyry-style mineralization is cross cut by the late stage low sulphidation type epithermal veins (Milu *et al.*, 2003).

Three exploration drill holes were investigated, which are located along a NW-SE profile across the mineralized porphyry intrusion and expose the system to the depth of 250 m from the surface. The cores represent distinctive parts of the porphyry system, with variable intrusive phases, alteration types, Cu/Au ratio and epithermal overprinting. Our scope was a detailed documentation of the magmatic phases, their specific mineral assemblages, the alteration features and the crosscutting relationships of the hydrothermal veins.

Based on the petrographical results, the studied zone of the Bolcana prospect is formed by successive porphyry phases of dioritic composition, which is locally associated with hydrothermal breccias, too. Considering the time relationships, there are two early phases, the medium grained porphyry (MGPO) and the coarse grained porphyry phases (CGPO), both suffered potassic alteration, overprinted by sericite(-chlorite) alteration. The medium grained porphyry (QMGPO) occurs as an intermediate phase, which was affected by a moderate sericite alteration. The late porphyry phase is the fine grained porphyry (FGPO) which suffered from a potassic alteration overprinted by a sericite-chlorite alteration and locally caused brecciation of the earlier intrusions. Locally the QMGPO suffered argillic alteration associated with hydrothermal brecciation. The host rock of the intrusions is a monomictic intrusive rock containing breccia (MXI) with propylitic alteration.

The hydrothermal alteration zones developed during the porphyry phases are accompanied by different vein types: M-type (magnetite), A1-type (quartz-magnetite), A2-type (quartz-magnetite-pyrite-chalcopryite-bornite), A3-type (quartz-pyrite-chalcopryite), D1-type (chalcopryite), D2-type (pyrite) and E-type (sphalerite, chalcopryite, pyrite, calcite) veins. Veinlet nomenclature follows (Gustafson & Quiroga 1975) and (Arancibia & Clark, 1996).

Fluid inclusion study was done on the quartz of the A2-type veinlets, as those veins contained appropriate host minerals and well preserved fluid inclusion assemblages. Four types of fluid

inclusions were identified: (1) halite-bearing polyphase fluid inclusions ( $S_H+L+V$ ), (2) fluid inclusions with other solid phase ( $S+L+V$ ), (3) two phase liquid+vapor with highly variable phase ratio ( $L+V$ ), (4) two phase ( $L+V$ ) fluid inclusions with fairly constant phase ratios arranged in plains. Types 1-3 occur in assemblages of primary inclusions, thus suggesting an inhomogeneous parent fluid, i. e. a boiling system, while type 4 is a secondary generation trapped from a homogeneous fluid. As the trapping of the primary fluid inclusions happened heterogeneously from an inhomogeneous system, the minimum homogenization temperatures ( $T_h$ ) of the aqueous liquid rich inclusions correspond to the formation temperature (Roedder, 1981). Thus, measurements done on the inclusions with  $V=10$  area% were taken into consideration.

Based on the results, the formation temperatures of the ( $L+V$ ) inclusions cover a wide range (140-280°C) while the ( $L+V$ +halite) inclusions homogenized at temperatures  $> 350^\circ\text{C}$ . The calculated salinities form two well distinguishable groups (0.5-5 NaCl equiv. wt% in  $L+V$  inclusions and  $\sim 33$  NaCl equiv. wt% in  $L+V$ +halite inclusions).

This deviation can be explained most likely by the fluidmixing, though the  $\text{CO}_2$ -clathrate formation upon cooling and the salinity increase during boiling may have also a slight effect on the calculated salinities.

The hematite in the inclusions proven by the Raman spectroscopy suggests the magmatic origin and oxidizing character of the mineralizing fluids (Henley *et al.*, 1984). The presence of  $\text{CaSO}_4$  as a solid phase in polyphase fluid inclusions shows the oxidizing character of the fluids and that the magma was saturated in sulphur (Lickfold *et al.*, 2003). The  $\text{CO}_2$  measured in the vapor rich inclusions is a typical component of the vapor phase after the boiling event (Webster & Mandeville, 2007).

The hydrothermal alteration types observed in the magmatic phases together with the occurrence of intermediate argillic type alteration zones suggest that the studied part represents most likely a shallow zone of a porphyry mineralization, though the observed low formation temperatures rise further questions, too.

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## Colour flints of Ukraine

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Flints are specific concretionary sedimentary solids, composed by authigenic aggregates of amorphous and crystalline silica. In the territory of Ukraine they are located in Volyn-Podillia, Donbas and the Crimea. Flint is the stone used by humans. First mentions on flints use are found in the Stone Age (Paleolithic). At that time it was used for making the first tools and hunting instruments, fire lighting, household keeping. In the Middle Ages flint was widely used in medicine. From historic sources it is known that in the 9<sup>th</sup> to 10<sup>th</sup> centuries in many countries of Europe flint was used for wall lining in premises, where meat was kept. For getting high-quality bakery flour flint grindstones were used at the mills. In German villages the pieces of crumbled flint were put into the tableware with milk for better keeping and prevention of early acescence. And up to nowadays flint is widely used as an efficient natural filter and water activator. Besides its curative phenomenon flint has rather peculiar physical-and-chemical properties (abrasivity, solidity, stability), due to this it is well handled - cut, ground, polished. Relative hardness at the Mohs Scale is 6.5-7. The hardness of flint is influenced by the presence of particles of organic substance or carbonate in it and also by the degree of devitrification of silica.

Our research concerns the study of flints from the point of view of their use in stone saw art. The main criteria for that is high ornamentality subject to texture and colour. Such forms allow producing different decorative goods from flints. Besides that it is necessary also to study technological aspects and conduct marketing research. We have carried out field studies of main forms of flints, considered the peculiarities of stratigraphic and regional extension, mode of occurrence and the morphology of flinty concretions. We have sampled a reference collection to determine the particularities of mineral composition, decorative and technological features and we have carried out in experiments.

The main concentrations of the stone are dedicated to deposits of the Upper Chalk, namely to the Cenomanian and Turonian. In these geological units they have almost regional extension. Flint manifestations are shown in the marine epicontinental facies, mostly composed of chalk, chalk whitestones and marls. Other facies types have sharply subordination sense. In the productive horizons the flints are present in the form of scattered-and-isolated concretions, sometimes they merge into coalescent flinty horizons, fixed on certain facies levels and they have regional distribution

The morphology of flinty concretions is rather variegated. The most popular ones are fanciful (bizarre), rarely they are roundish and isometric. Flints joined into the horizons as a rule have a plate-like flattened shape. The sizes of the concretions vary from several mm to 80 cm in diameter, the weight is ranging from several grams to 30 kg. The surface of the flints is irregularly humpy with numerous hollowness and salience. The contact of flints with the enclosing rock is always clear, on the top the flints are covered with white crust.

Mineral composition of concretion silicstones among studied manifestations is rather homogeneous. They are mostly (90-95%) composed of cryptocrystalline chalcedony and small amounts (5-10%) of quartz, opal, sulphides, oxides and hydroxides of iron, calcites, coaly material and organic remains.

Flints are very different in colour - black, grey, dark grey, blue-and grey, red, brown, light brown, yellow-and-brown, yellow ones. The nature of flint colours is allochromatic. Colours from yellow to brown is caused by the presence of oxidized forms of iron, blue-and-grey colours - by iron oxides, and dark grey and black - by presence of coaly and organic material. By their texture the flints can be one-colour, concentric-and-zonal, patterned and spotted.

We have technologically developed decorative goods and jewellery from material of selected reference collection of flints (taking into consideration their features): a jewel case, buttons, a tieclasp, a penholder, a pendent and others (Fig. 1.).



Fig. 1.: Decorative goods and jewellery made of Ukrainian flint. Flint wares have not only aesthetic look but they are ecologically safe.

As a conclusion we can say that the flint can be effectively used in different spheres as abrasive and jewel-and-productive material. The most part of colour flints on manifestations can be gathered from the surface that is economically sound.



## Stability of Colloidal Bentonite Particles in Aqueous Systems

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Deep geological repositories are one of the preferred alternatives for the safe disposal of a high-level radioactive waste in many countries. The repository consists on a multi-barrier system. Bentonite is considered to be a suitable material as one of the barriers mainly because of its swelling and sorption capacity and low hydraulic permeability. However many experiments have shown that during bentonite-water interaction colloids may be formed (Missana *et al.*, 2011; Arcos *et al.*, 2003). For safety assessment is essential to study the stability of these colloids, because stable and mobile colloids may cause increased migration of radionuclides, compromise the functionality of the bentonite barrier.

The objective of this study was to investigate the stability of bentonite colloids during the interaction of bentonite with water under different conditions. Classical sedimentation tests are an easy method for studying the colloidal stability.

The laboratory tests were performed using Czech Sabil bentonite, which is Na-activated type of bentonite. The suspension of bentonite and deionized water with S:L = 1:180 was prepared in glass cylinder and was sampled at regular intervals from the level of the selected reference point. The concentration of sedimented colloidal particles in the suspension and their time evolution was measured. There were studied the effect of bentonite saturation time, the concentration of electrolyte (NaCl) and type of the electrolyte (KCl, CaCl<sub>2</sub>, MgCl<sub>2</sub>) on the stability of colloidal particles. The research was carried out at room temperature and the sedimentation of particles was measured at an interval of 1 week to 5 months.

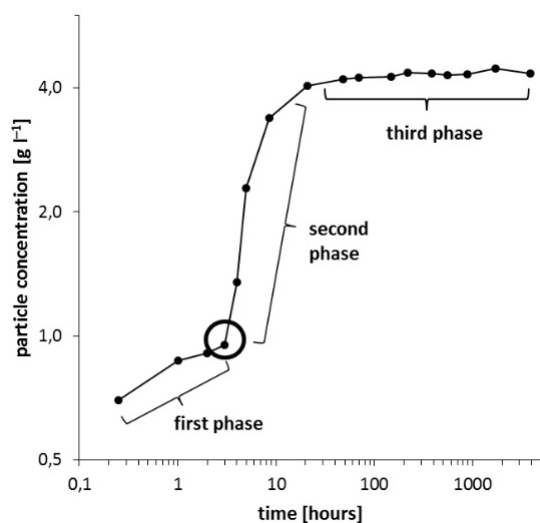


Fig. 1: Particle concentration as a function of time with indicated phases of sedimentation. The circle shows the beginning of the second phase. Both axes have a logarithmic scale.

The experimental results demonstrate that sedimentation of bentonite particles occurs in three phases and all phases are influenced by the bentonite saturation time, by the concentration of NaCl and by the type of the electrolyte. The most significant point on the all curves is

the beginning of the second phase, which corresponds to the rapidly increasing concentration of sedimented particles (Fig. 1). For this reason, the effect of different conditions on the stability of particles is the most evident at this point.

Adding NaCl causes the second phase to come earlier compared to simple sedimentation – the higher the concentration of NaCl, the sooner the second phase begins. The stability of bentonite particles decreases with increasing concentration of NaCl (Fig. 2).

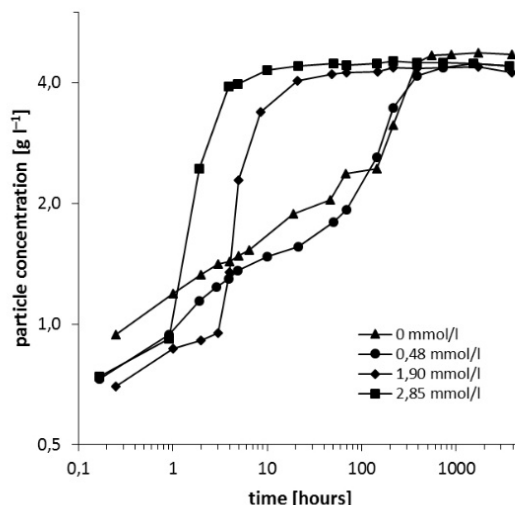


Fig. 2: Particle concentration as a function of time in experiment with the increasing concentration of NaCl. Each curve represents different concentration of NaCl. Both axes have a logarithmic scale.

In the case of bentonite saturation time, experiments were performed in two series – as simple sedimentation with no additives and with the addition of the same concentration of NaCl. In the series with added NaCl, the start of the second phase is directly proportional to the bentonite saturation time, but inversely proportional to the bentonite saturation time for simple sedimentation. In the case of the simple sedimentation, the stability of particles decreases with increasing saturation time and in experiments with added NaCl decreases with decreasing saturation time. The stability of colloidal particles is also influenced by the type of electrolyte. Adding of KCl and MgCl<sub>2</sub> causes the decrease of the colloidal stability.

During sedimentation of bentonite colloids several layers in suspension were formed. The granulometric analyses have shown that the layers have significantly different particle size and concentration. Over time the layers are moved downward by gravity and it was found that the beginning of the second phase is related to the transition of one of the concentration boundary between two layers through sampling point level.

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# Variability, ecology and paleoecology of the species *Cycloforina cristata* (Millett)

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In this research we have carried out of micropaleontological studies in the Rădăuți area (Suceava County) where we have identified 25 specimens of *Cycloforina cristata* (Millett), species which has not been mentioned in Sarmatian deposits from Moldavian Platform (Northeast România, Fig. 1).

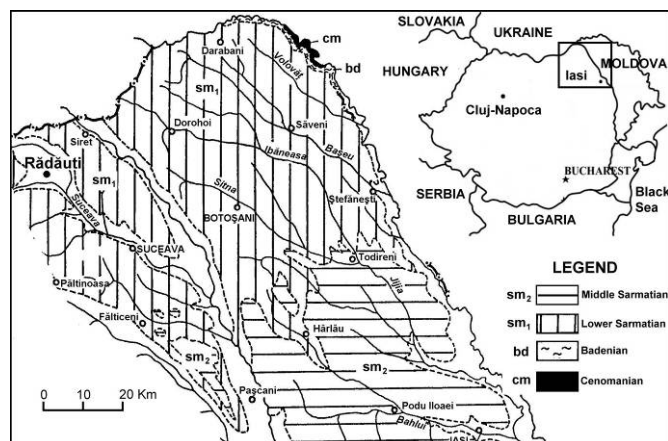


Fig. 1: Geological map of the studied area (after Ionesi *et al.*, 2005)

Until now, this species has been mentioned in a small number in Sarmatian deposits from Zrecze, Poland (5 specimens, Łuczkowska, 1974), Făget Depression (Popescu, 1995) and from the southern part of the Vienna Basin (5 specimens, Schütz *et al.*, 2007). The authors have attributing this species to the genus *Cycloforina*. In the studied sediments, this taxon is very rare. Millett (1898) identified one specimen (the holotype) in the Malay Archipelago, classified it into genus *Miliolina*. Later, this foraminifer was found by Seiglie (5 specimens, 1966, 1967 fide Culver & Buzas, 1982) in the shelf sediments from Araya – Los Testigos, (Caribbean Sea), Seibold (1975) in the nearshore area of Cochin (southwest India), Rao *et al.* (15 specimens, 2005) in the Bay of Bengal and Suresh *et al.* (2013) identified this species in the estuary sediments from Chennai. The last two locations are situated on the southeast coast of India. All the authors which have identified this species in the recent sediments attribute it to the genus *Quinqueloculina*.

The relatively large number of the specimens found allowed us to study the variability of this species. It's not noticeable major differences regarding the dimensions of the specimens found instead the morphology of the test presents an extremely large variability. Some specimens have strongly, quasi – evenly serrated edges, while the others have weak or unequally distributed spines (Fig. 2). Based on the comparison with the recent specimens found by Rao *et al.* (2005) we could declare that the recent and Miocene specimens are quite similar.

In this study we discuss some aspects regarding the ecology of the recent specimens based, on the data published in the literature. References about live specimens, doesn't exist, only informations about the conditions where the empty test of this foraminifers were found.

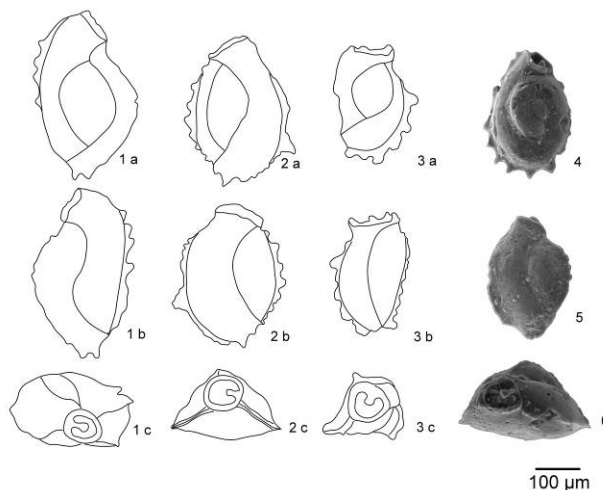


Fig. 2: Morphological variability of *Cycloforina cristata* (Millett): 1a, 2a, 3a, 4 – front side; 1b, 2b, 3b, 5 – back side; 1c, 2c, 3c, 6 – apertural view.

Most of them have been identified in sandy deposits from the shelf, lagoon or estuary area, with normal or lower water salinities.

Regarding the paleoecology of the species *C. cristata*, we take into consideration the fact that the most of the fossil specimens were found in clay deposits, in a faunistic association (*Inaequicostata inopinata* (Grishkevich), *Mohrensternia inflata* (Hoernes), *Cycloforina karreri karreri* (Reuss), *Elphidiella serena* (Vengilinski), *Elphidium reginum* (d'Orbigny)) typical for the Early Sarmatian.

We discuss some issues regarding the water salinity of the basin were this foraminifers may have lived, based on the data existing in the literature (Papp, 1956; Ionesi, 1968; Ionesi *et al.*, 2005; Piller & Harzhauser, 2005; Studencka & Jasionowski, 2011).

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## Tectonics in salt deposits – a challenge in exploration and mining

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The influence of tectonic structures on salt deposits in terms of exploration and mining shall be introduced using the example of a potash deposit in Central Germany which is affected by Miocene volcanism.

This potash deposit has a Permian (Zechstein) age. The deposit is part of the Central European Basin and dominated by several syn- and anticlines. The Zechstein formations are overlain by up to 1.000 m of Triassic sandstone and partially by limestone. Therefore the bedrock is tripartite into an under- and overlying competent part and incompetent salt in between. Correspondingly to this fact the rock mass reacts differently under tectonic stress (Hessmann & Schwandt, 1981). The focus in this paper lies on the salt formation that is characterized by halokinetic and halotectonic movements caused by overburden load (pressure) and tectonic impulses. There have been several tectonic phases during the Mesozoic and Cenozoic with different influence on the deposit.

Carnallite deformation is common in potash seams showing thickening, thinning and fold structures because of different properties of carnallite, sylvite and halite. Water-containing minerals, as for example carnallite, are the most mobile. Halite shows lower viscoplasticity, while anhydrite reacts as nearly solid rock (Schwandt, 2005). Internal dissolution and recrystallization processes dominate metamorphosis which is leading to various facies associations within the potash seams. The majority of brines occurring in the deposit are the result of solution metamorphism, or in rare cases, they are connate water (Herbert *et al.* 2007). Connate water can derive from the cap rock or the basement.

The youngest tectonic influence on the deposit is caused by Miocene basalts which lead to extensive mineral reactions within the potash seams (Fig. 1). The intrusion of basaltic dykes in the Zechstein evaporates yielded to rigid behaviour of the salt and created subparallel trending joints with varying thicknesses from < 1 mm to > 30 mm. They can either be mineralized by halite, sylvite or carnallite or occur as basalt dyke (Jahne *et al.* 1983, Hessmann & Schwandt 1981). Because of a fast cooling illustrated by an up to mm-thick glass coat the boundary between rock salt and basalt is very sharp. So in most cases there are no interactions between halite and basalt. Preliminary geochemical investigations of the basalts show that most volcanic rocks are foidites.

Near the basalts so called “crystal salt” is common. It is coarse grained halite indicating a recrystallization due to water supply. These zones of depletion are framed by sylvite and carnallite (Fig. 1). In rare cases small crevices remain in the salt and are preserved, e.g. an open dry cave of about 100 m<sup>3</sup>, described by Pippig (1992).

Mining under all those circumstances requires exploration programs to determine the composition of potash seams and to minimize the risk potential caused by basaltic dykes and big fault zones which are sometimes connected with formation fluids. For all

those reasons a geological model has to be established and updated. Therefore several data have to be taken into account. Those include drillings from surface and underground, seismic and ground radar data as well as magnetic and gravimetric perceptions.

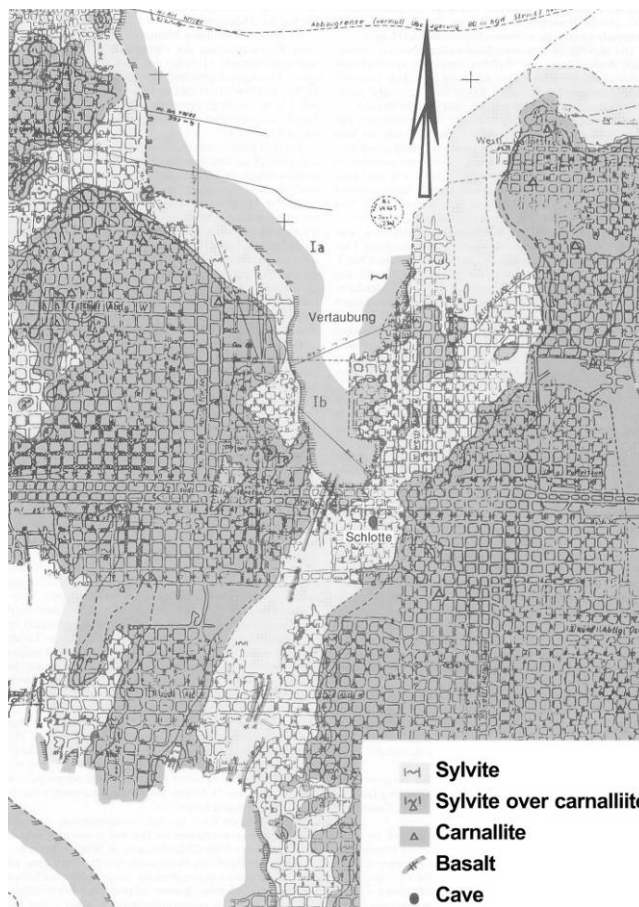


Fig. 1.: Lithofacies along basalt dyke, Pippig (1992)

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Distribution of  $^{226}\text{Ra}$  in the surface soil in the vicinity of the thermal power plant Plomin (Croatia)Gorana Ernečić<sup>1</sup>, Ivanka Lovrenčić Mikelić<sup>2</sup>, Gordana Medunić<sup>1</sup><sup>1</sup>Faculty of Science, University of Zagreb, Zagreb, Croatia (gernecic@gmail.com)<sup>2</sup>Laboratory for Radioecology, Ruder Bošković Institute, Zagreb, Croatia

Purpose of this study was to determine the long term influence of the thermal power plant (TPP) Plomin in Istria peninsula (Croatia) on the possible contamination of the surrounding soil by the radionuclides from the emitted coal ash. Coal naturally contains radionuclides of the  $^{238}\text{U}$  and  $^{232}\text{Th}$  decay series, as well as  $^{40}\text{K}$ , which concentrate in ash due to coal combustion, several times more in comparison with their content in coal or surface soil (Dai *et al.*, 2007). This preliminary study will focus only on the  $^{226}\text{Ra}$  which is, along with its decay products, responsible for the largest part of the dose received by humans from the naturally occurring radionuclides.  $^{226}\text{Ra}$  is an alpha emitter with a half-life of 1622 years. It has similar chemical characteristics to calcium which can lead to calcium replacement in bones if it enters in an organism and is therefore harmful for people. Furthermore,  $^{226}\text{Ra}$  decays to  $^{222}\text{Rn}$ , with a half-life of 3.8 days, which is a noble gas and can easily be inhaled into the human organism, known for causing lung cancer (Eisenbud & Gesell, 1997).

The main assumption of this research was that radionuclides could be dispersed into the environment from the plant stack and from the ash piles next to the TPP due to the rainfall and the wind flow. Considering that  $^{226}\text{Ra}$  is a terrestrial radionuclide, present in all rocks and soils in variable amounts, the main purpose was to evaluate if the natural radioactivity of the area was elevated due to influence of the flying ash and/or bottom ash produced by the coal combustion. The results were compared with the control sample and with the average soil value.

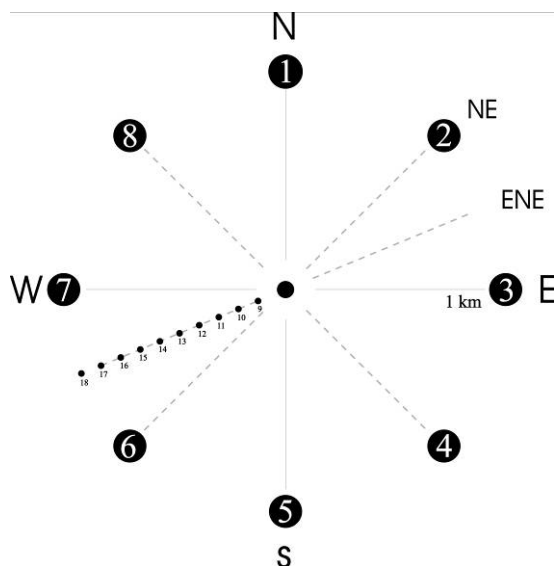


Fig. 1.: Sampling grid around the Plomin thermal power plant

Soil samples were collected around the TPP at 18 sampling stations from the surface soil layer, 0 – 10 cm depth. (Fig. 1.). Eight samples were radially collected at 1 km distance from the plant, and 10 soil samples were collected within 1 km distance every 100 m along the profile located in the prevailing wind direction (NE, ENE). Also, one control sample (K1) was collected, about 10 km away from the

plant. All soil samples were of the same rock type, which is limestone (Šikić & Polšak, 1973).  $^{226}\text{Ra}$  massic activity in soil samples was measured using gamma-ray spectrometry system with the HPGe detector and 609.3 keV line of its progeny  $^{214}\text{Bi}$  was used to determine  $^{226}\text{Ra}$  massic activity.

Sample identification	$a(^{226}\text{Ra})$ (Bq/kg)	Sample identification	$a(^{226}\text{Ra})$ (Bq/kg)
1	67.5	11	190
2	30.6	12	130
3	53.4	13	121
4	106	14	167
5	72.1	15	157
6	581	16	172
7	90.2	17	120
8	96.9	18	64.5
9	202	K1	105
10	127		

Table 1.  $^{226}\text{Ra}$  massic activities in the soil samples

$^{226}\text{Ra}$  massic activities in the soil samples (Table 1.) ranged between 30.6 Bq/kg and 581 Bq/kg with the mean value 142 Bq/kg. In all samples, except in sample 2, including the control sample,  $^{226}\text{Ra}$  massic activities were increased compared to the world average of 40 Bq/kg (UNSCEAR, 1993), probably due to generally higher  $^{226}\text{Ra}$  massic activities in carbonates (Coward & Burnett, 1994). Samples at 1 km distance from the plant showed mainly lower  $^{226}\text{Ra}$  massic activities than the control sample which points to the soil heterogeneity and the need to collect more control samples to obtain more representative control value. Samples within 1 km distance from the plant showed higher massic activities.  $^{226}\text{Ra}$  massic activities in the samples within 1 km distance from the plant were higher than massic activities in the samples at 1 km distance and were generally decreasing with increased distance from the plant. Samples located NE from the plant (samples 1, 2, 3) showed lower activities than samples located on the SW (samples 5, 6, 7), with sample 6 showing four times higher  $^{226}\text{Ra}$  massic activity than the average of all samples. The latter could be explained by the influence of the prevailing winds.

Increase of  $^{226}\text{Ra}$  massic activities in the surface soil around the TPP could be related with the coal combustion. Moreover, the prevailing winds significantly affect the  $^{226}\text{Ra}$  distribution in the soil. It should be noted that these are only preliminary results and further analyses will be taken to make more conclusions.

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# Compositional zoning in pyrite as a tool for reconstructing the ore ore-forming processes: an example from the abandoned Fe-Cu sulfide mine of Herin (Aosta Valley, Italy)

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The Herin abandoned mine (Champdepraz, Aosta, Italy) was exploited for at least 250 years for its Cu-Fe sulphide ore. It is located at the orographic right of the Aosta Valley, approximately between 1600 and 1800 m a.s.l.. Host rocks belong to a metaophiolitic domain of the Western Alps that underwent high pressure metamorphism, and re-equilibrated under blueschist to greenschist facies conditions (Martin *et al.*, 2004; Dal Piaz *et al.*, 2010). Ore association is mostly composed of pyrite and chalcopyrite, with minor other sulfides (pyrrhotite, sphalerite, cubanite, digenite) and oxides (magnetite, rutile, ilmenite). The sulfide ore occurs with zoned textural patterns, from massive to disseminated. The deposit consists of lenticular massive bodies and thin layers hosted in various greenschist facies metamorphosed lithotypes. Some preserved slug dumps and mining structures document an intense exploitation. Thus, the interest for this site is aroused mainly by the lack of modern studies on the mineralisation, but also by the potential of an environmental recovery and cultural evaluation of the site.

The aim of our work is to document the overall state of the mine and to give interpretation of the ore genetic processes. We gathered historical information about the exploitation and mapped the underground works with speleological tools. Moreover, we collected data on mineralogy, mineral chemistry, petrography on mineralized samples. The mineralogical and textural study was conducted by optical transmitted and reflected light microscopy. We undertook electron microprobe spot analyses (EMPA) on single grains of the ore minerals, as well as of the gangue and the host rock minerals. Besides, we performed elemental mapping on single grains or pyrite, representative of its various textures. On the basis of previous works and our results, we identified two parameters as the driving criteria for a comprehension of the multistage process that led to the actual configuration of the ore: (a) the textural characters of pyrite and (b) the distribution of trace elements in sulfides, with specific focus on cobalt and nickel in pyrite.

Because of its refractory nature, pyrite is in fact known to preserve changes that occurred during its growth history, such as multiple episodes of metamorphic/hydrothermal activity, or the chemical evolution of the fluid during a single episode (Craig *et al.*, 1998). In particular, the concentration of cobalt and nickel and the Co/Ni ratio in pyrite have extensively been used as indicators of primary genesis and tools for reconstructing the ore forming systems (Bralia *et al.*, 1979; Campbell & Ethier, 1984; Agangi *et al.*, 2013).

The coupled use of spot analysis and atomic maps (Fig. 1) provides an integration of the textural and geochemical sets of data. The concentration data show a zoned distribution of cobalt in pyrite

that can be related to typical recrystallization textures. We determined a critical concentration value for cobalt of 3160 ppm, as a discrimination point between two generations of pyrite. This led to outline a series of dissolution and crystallization events that describes the metamorphic history of the sulfide ore at the sample-scale. Moreover, on the basis of the Co/Ni ratio we propose a volcanogenic-hydrothermal origin for the first generation of pyrite, thus for the primary deposition of the Herin ore deposit.

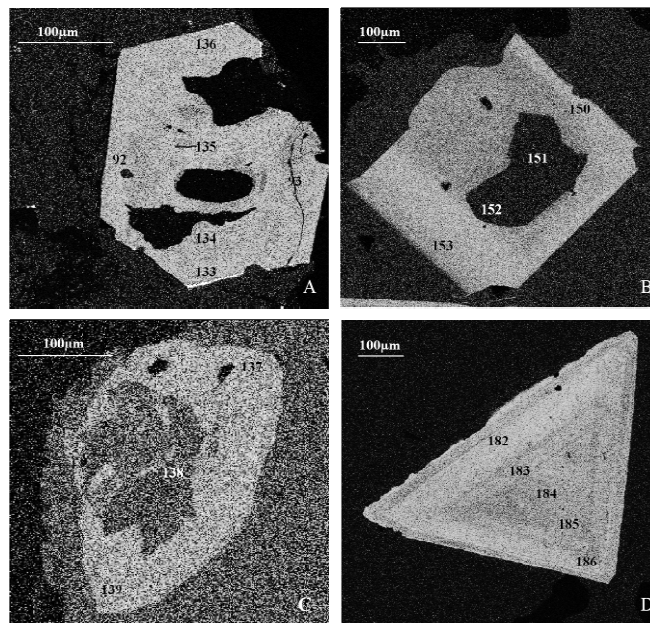


Figure 1.: Atomic EMP maps of Co. Some recrystallization textures of pyrite are represented. The numbers refer to the punctual analysis series.

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## Lithology of Lower Cretaceous “Urgonian” Carbonate Platform Facies in the Manín Unit (Western Carpathians)

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The term “Urgonian facies” refers in the Western Carpathians to massive organodetrital limestone with Upper Barremian–Aptian fossil remains. From bioclasts, fragments of rudistid bivalves, echinoid particles, foraminifers (*Palorbitolina lenticularis*, *Sabaudia minuta*), coralline algae, bryozoans, fragments of hydrozoa are most characteristic. Their occurrences in the Western Carpathians were processed and summarized by Mišík (1990). During the Barremian–Aptian a carbonate platform evolved near the northern margin of the Central-Carpathian Block in accordance with the widespread platforms of Urgonian type in Tethys realm. Two centres can be traced in Western Carpathians: the Tatric Urgonian platform (biohermal and lagoonal facies), from where detritus was transported into the Muráň limestone and the Manín Urgonian platform prograding into Belá succession during Aptian. Debris from both centres was transported into adjacent basins and laid down as allodapic accumulations.

The Manín Unit is originally Central Carpathian unit which has become a part of accretionary prism in the front of Central Carpathian block. It was incorporated into the region of the Pieniny Klippen Belt. It was deformed during the younger phases of the Alpine Orogeny together with the Outer Carpathians.

In the Butkov Quarry a sequence of the Lower Jurassic and Lower Cretaceous beds of Manín Unit was exposed. Urgonian complex consists of the thick bedded Podhorie Formation and of the massive Manín Formation. The Podhorie Formation consists of Barremian to Lower Aptian organodetritic as well as micritic limestone with chert, rarely with fragments of basic extrusive rocks. The formation reaches thickness of 65 – 75 m. Upwards they pass into the carbonate platform limestone of the Manín Formation. It is developed in complex of mainly gray to light gray massive organogenic limestone with numerous Aptian to Albian fossils: foraminifers (*Orbitolina*), crinoids, echinoids, molluscs, ostracods, corals and calcareous algae. Total thickness of the formation attains around 50 meters. The Manín Formation is terminated by hardground surface, which is followed by deep-sea clay sediments of the Albian - Cenomanian Butkov Formation (Borza *et al.*, 1987). This “Urgonian” carbonate complex of biotrititic and biogenic limestone of shallow-sea carbonate platform origin gradually covered the basinal deposits of the region. In the Butkov area, the major part of these carbonates is developed as the carbonate platform facies and its slope (Michalík *et al.*, 2005).

Urgonian limestone in the Manín Straits represents a typical member of the bed sequence of the Manín Unit (Mišík, 1990). Only

Barremian strata are represented here, upper part of the sequence was eroded before Albian. The limestone is massive organogenic to gravelous, in the uppermost parts rudist (only fragments) limestone occur and look like from reef core being bioclastic without corals and terrigenous admixture. Thickness of the limestone reaches 90 m.

The “Urgonian” facies of the Skalica Klippe near Dolný Moštenec village (Strážovské Vrchy Mts.) is represented by coarse-grained carbonate conglomerates and breccias about 17 m thick, composed of “Urgonian” limestone clasts (Michalík *et al.*, 1984). Several cycles have been recognized within the sequence. The stratigraphical range from Middle Aptian to the boundary Aptian–Albian was ascertained with microorganisms and two cephalopod horizons. The sequence is overlain by dark Albian limestone with chert. All pebbles as well as angular clasts within the “Urgonian” facies belong to Barremian–Aptian rocks, mainly typical “Urgonian” organodetrital limestone considered as debris flows in channels on the foot of steep submarine elevation.

Nížná limestone is related to the Manín Unit folded later into the Pieniny Klippen Belt (Orava area) (Mišík, 1990). It is composed of Barremian–Aptian organodetrital limestone. The basal part contains breccia with the fragments of Upper Jurassic–Lower Cretaceous limestone, black chert and marl. This “Urgonian” limestone locally contains brownish chert, too. Associations of bivalves, echinoderms, agglutinated foraminifer (*Hedbergella*), echinoid spines and coralline algae are the most frequent. Estimated thickness reaches 10 m.

The Haligovce Klippe is usually considered as an equivalent of the Manín Unit (Birkenmajer, 1977). This limestone of “Urgonian” type is 40 m thick. Its lower part is formed by bituminous, thick bedded limestone with chert, the upper part of the sequence is formed by light-grey massive organodetrital limestone with pelecypod detritus, fragments of foraminifers (*Orbitolina*), plates of echinoderms and scarce bryozoans.

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# Palaeontological analysis of Middle Miocene siltstone from outcrop in Wiślica (Carpathian Foredeep, Central Poland)

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The Carpathian Foredeep is a youngest tectonic unit of Poland occupies the area between the Outer Carpathians and the Mid-Polish Uplands. Origin of the Carpathian Foredeep is directly connected with the Outer Carpathians evolution (details in: Oszczytko, 2006). The Carpathian Foredeep basin was a part of the Central Paratethys which was the northern part of the disappearing Tethys Ocean. This part of the Paratethys sea was the northernmost part of the basin. Central part of The Carpathian Foredeep is filled with Miocene siliciclastic molasse with evaporites. Sediments near the margins, especially in the North of the basin are much more diverse. The axis of the sedimentary foredeep basin was moving from the south to the north during the Miocene time. The deposits of the Carpathian Foredeep cover different older rocks (e.g. Radwański, 1973).

The Middle Miocene deposits in the Wiślica region are represented mainly by gypsum of evaporitic stage - Evaporitic-Chemical Beds (Krzyżanowice Formation, Wielician) and mudstones above and below them (Alexandrowicz *et al.*, 1982).

Geographically, Wiślica (GPS coordinates: N 50° 21' 35,4"; E 20° 41'5,5") is located in Małopolska Upland, in Nida Basin. The outcrop of the studied mudstone series is located near the cemetery, in the outskirts of the town. The Miocene deposits presumably covered the Upper Cretaceous marls. However, there is no evidence for the age of the basement so far. The Middle Miocene section begins with a thin layer (thickness varies) of basal conglomerate. Above the conglomerate lies a series of mostly horizontally laminated mudstone. The deposit contain bivalves, such as oysters (*Pycnodonte* sp.) and scallops (*Amusium* sp., *Aequipecten* sp.), besides diverse microfossils. Micropalaeontological analysis has revealed that deposits are foraminiferous. Both benthic and planktonic foraminifers occur. Agglutinated species are relatively uncommon. Insignificantly more common are planktonic foraminifers, mainly from Globigerinidae group, *Orbulina* genus. The following taxa of benthonic foraminifers were identified:

*Dentalina* sp., *Dentalina emaciata* Reuss, 1851, *Lenticulina* sp., *Uvigerina* sp., *Nodosaria* sp., *Nonionella atlantica* Cushman, 1947, *Stilostomella lepidula* (Schwager, 1866), *Bolivina* sp., *?Cibicides* sp., *Marginulinopsis* sp., *Marginulina* sp. Among those taxa predominant are: *Uvigerina* sp., *Dentalina* sp., *Lenticulina* sp., *Nodosaria* sp. Moreover, the deposit contains numerous remains of Osteichthyes (bony fish), especially otoliths and rarely vertebrae and teeth. Lots of urchins spines, ostracods and some bryozoans are also recognised.

Abundance of microfossils and their variability suggest advantageous environmental conditions for life for many groups of organisms. The presence of Pectenids, echinoderms and planktonic foraminifers points to normal salinity (e.g. Szczuchura, 1982; Studencka, 1999). Presence of these fossils suggests the Badenian age, according to widely accepted fact that salinity decreased at the Badenian-Sarmatian boundary (e.g. Oszczytko, 2001). Transgressive nature of the studied deposits that begins with conglomerate suggests the Late Badenian age, after the evaporation period. Sea level of Paratethys during the evaporation period was low and had increased after that (Rögl, 1998). The evaporation period is traditionally assumed to Middle Badenian, but according to Oszczytko (2001) to Upper Badenian.

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## **Gasometric Anomalies in Bottom Sediments of the Western and Central Barents Sea: a preliminary data report**

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Bottom sampling in several areas of the Barents Sea and sub-sampling of hydrocarbon gases from collected sediments were carried out as part of various geological marine expeditions. These expeditions were organized by the UNESCO-MSU Training and Research Centre for Marine Geology and Geophysics of the Moscow State University (Russia) and the University of Tromsø (Norway) onboard R/V «Akademik Nikolaj Strakhov» and R/V “Helmer Hanssen” during the period of 2011-2013.

A total of 304 gas samples from 51 different stations were analysed using Gas Chromatography (GC) and Isotope Ratio Mass-Spectrometry (IRMS) techniques. These were combined in a database which was used to investigate the relationship between the type of the depositional environment, hydrocarbon gas concentration and sediment composition.

Gas samples, collected from shelf deposits, consist mainly of methane (90-99%) with little admixture of ethane and propane. Unsaturated homologues were detected in all samples. Ethylene and propylene predominate over saturated homologues. This, together with the isotopic composition, suggests a biogenic nature of the gases collected in most areas.

Gas concentrations were found to be very low for the majority of analysed sediment samples. This is indicative for their low filtration capacity and low organic matter content. The cause of this is believed to be the pelitic clayey composition of the sediments, their high compaction and the generally frugal bioproductivity in arctic regions.

The specific molecular and isotopic composition and the high concentrations of gas are characteristic for the zones of focused hydrocarbon seepage on the seafloor that were studied during the cruises. Areas with pockmarks, outcropping salt diapirs and gas flares above the seafloor were classified high petroleum potentials, such as the Hjalmar Johansen High and the North-Kildenskoe gas field, were examined in order to verify characteristics of gas emission from deeply seated accumulations of natural hydrocarbon. This showed that even in such areas the background gas seepage is insignificant and anomalous gas concentration were detected only in fault zones according to the results of the gas analyses.

The uppermost sedimentary cover has a strong effect on deep fluid seepage in the Barents Sea region, both in regular areas and at locations with highly focused flows.

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## **The shape of the bases of turbiditic sandstone beds versus the underlying fine-grained sediments' features and their foraminifer content: an example from the Magura Beds in Ropica Górna area**

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The research regarded sediments from the Magura Nappe in the Polish Outer Carpathians deposited during the Eocene-Oligocene transition. It investigated the relation between the shape of the base of turbiditic sandstone beds and the features of underlying fine-grained sediments, in particular their foraminifer content and distribution. The carbonate, sand fraction and quartz grains content in mudstones were other analysed features. An important aspect of the research was to examine the vertical changes in these features, as well as to observe the relation between these changes and the type of the overlying sandstone bed bottom.

Two types of bed bases have been distinguished; flat and irregular, and three classes of bed thicknesses have been established; thin (<10 cm), medium (10-30 cm) and thick (>30 cm). Considering the above criteria 10 cases of sandstone and underlying mudstone have been chosen from which the total number of 26 samples of fine grained deposit was taken. Each case has been analysed by taking 2-3 samples directly from under the sandstone base in various distances. One case was considered for both flat and irregular medium thickness sandstone beds, while two examples have been investigated for thin and thick bedded sandstones with different base types. In order to examine the mudstone sand fraction components the samples have been disintegrated by liquid nitrogen method and the carbonate content has been obtained using Eijkelkamp calcimeter (08.35).

All data have been presented in the chart with sample order corresponding to the outcrop setting; therefore the changes in the analysed features were clearly visible. The large number of foraminifer has been observed both in turbiditic and non-turbiditic

shale. The general trend of decreasing carbonate content towards the mudstone top with concurrent increase of foraminifer content was clearly noticeable. The greater amount of a was most of the time related to higher amounts of agglutinated foraminifer instead of calcareous benthic and planktic foraminifer. The analysis of sand fraction content in shale showed in four cases increasing trend towards the mudstone top and in two cases decreasing pattern and no trend was observed for the remaining cases. Similarly for five cases the increase of quartz grains content towards the mudstone top was detected. Moreover glauconite occurrence was more common in samples taken from the top parts of fine-grained sediments overlain by thick sandstone beds. No relation between the shale carbonate content, as well as its foraminifer amount and the type of the sandstone bed base was observed.

Four samples representing interturbidite have been identified. Three of them were taken below sandstones with flat bed base and one came from the sediment underlying sandstone bed with irregular base. It may indicate that the turbidity currents resulting in flat bed bottoms have smaller erosional potential. It is worth mentioning that interturbidite appearance was related to thin and medium bed sandstones, which, together with other features of fine-grained sediments especially their foraminifer distribution, suggest a stronger rate of erosion by sedimentation of sandstone beds with larger thickness.

Remin, Z., Dubicka, Z., Kozłowska, A., Kuchta, B. (2012): *Marine Micropaleont.* 86-87: 11–14.

# Analytical and numerical evaluation of pumping test data in carbonate aquifers of the Buda Thermal Karst, Hungary

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The revision of archive well hydraulic data is significant for regions where limited pumping test data are available, like the area of Budapest. Interpretation of hydraulic parameters ( $T$ ,  $S$ ) based on well tests may be used as input data in hydrostratigraphic evaluation of the rock framework for numerical simulation. The geological logs and documentations of the pumping test data were collected and digitalized for thermal wells of the area of Buda Thermal Karst.

The modern hydrogeology defines the representative elementary volume (REV) for which the hydraulic parameters have to be considered as constant. Since that it has known that the value of hydraulic parameters depends on the scale of the examination. The carbonate aquifers can be characterized from fractured to hierarchical permeability structures. Therefore their hydraulic conductivity highly depends on the scale of the evaluation.

Different methods can produce  $T$ ,  $S$  values which are representative for different volume of rock. Short term pumping test can produce values for the limited zone in the surroundings of wells, while long term pumping data can be representative for the bigger rock volume. For carbonate aquifers with high level of heterogeneity the representativity of the data derived from pumping test is highly depends on the length of pumping tests (Király, 1975).

The goals of the study were the re-evaluation of the pumping test data for the carbonate aquifer system of Buda Thermal Karst: i) to compare the parameters derived from single pumping test data and an interference test; ii) to evaluate the effect of double porosity of carbonate aquifers on hydraulic parameters ( $K$ ,  $T$  and  $S$ ); iii) to compare the efficiency of analytical and numerical methods in the evaluation.

The processed data series were partly short term recovery tests which originate from well tests during establishment of new wells. In the second part of the evaluation a unique large-scale long term interference test was reinterpreted, which were performed after establishment the Pascal thermal well in 1966 (Böcker, 1966).

Classical analytical and numerical methods were used respectively. The applied analytical method based on the Theis-Jacob recovery test and for the evaluation the Aquitest software was used. The Visual Two-Zone model and the WT model (Székely, 2006) were applied for numerical simulation of the data for the carbonate sequence. These softwares handles the heterogeneity as anisotropy. The derived hydraulic parameters from analytical and numerical solutions and from short and longer term tests were compared in the study.

The significance of the research is that the available data of thermal wells for the area of Budapest were re-evaluated. During the research 21 single well pumping test data series were analysed. However in several cases the missing records of the measurements made the evaluation impossible. The revision was made with the Cooper-Jacob analytic method in local and regional scale (Pascal long term pumping test) too. Finally numerical simulation was used for 4 wells to obtain the required hydraulic parameters (Fig. 1). As a conclusion of the study the Upper Triassic Dolomite

(Hauptdolomit) can be characterized by  $K_h=10^{-5}$  m/s,  $K_v=10^{-2}$  m/s average hydraulic conductivity value, while the Middle Triassic Dolomite by  $K_h=10^{-5}$  m/s,  $K_v=10^{-3}$  m/s values, but for this formation only one data set was available.

The numerical revision of the archive pumping tests has a great value, because repeating these tests on the present price, would be very expensive, 1500-5000 EUR per well.

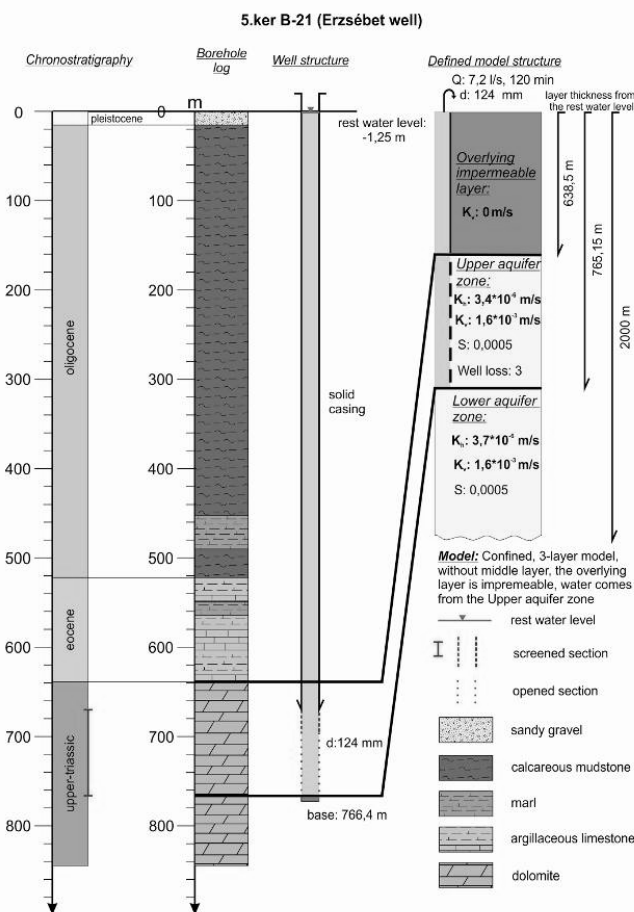


Fig. 1.: An example for the numerical model (B-21 well)

Böcker, T. (1966): A Pascal-malmi termálkút folyamatos kompresszorozása és annak hatása a budapesti termálkutakra, VITUKI Témabeszámoló Kézirat (manuscript, in Hungarian)

Király L. (1975): Rapport sur l'état actuel des connaissances dans le domaine des caractères physiques des roches karstiques. In: Burger, A., Dubert, L. (eds.), Hydrogeology of karstic terrains, Int Union of Geol Sci, B, 3:53-67

Székely F., (2006): A háromdimenziós kúhidraulikai modellezési módszer és gyakorlati alkalmazása. VITUKI Közlemények 79.

The research was carried out in the frame of an OTKA project (NC 101356).

## Detection of Gossans in Sonora (Mexico) with the Use of Remote Sensing Techniques

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Gossans and alteration zones often led to economic concentrations of metals. Their detection on satellite images, which is the aim of this study, can help in prospecting for metal deposits, especially in relatively unexplored areas. Also, the study attempted to find the methods which would be optimal for obtaining geological information from remotely sensed imagery on territories with similar climatic, geological, and topographical characteristics.

The field of the study is located in Sonora (NW state of Mexico), about 140 km NE of state's capital city of Hermosillo, and it is a rectangle of the area about 700 km<sup>2</sup>. It lies in the Basin and Range Province, which is mainly composed of late-Cretaceous - Miocene volcano-sedimentary sequences forming elevations and poorly consolidated Pliocene and younger sedimentary rocks filling valleys. Locally, there are outcrops of Laramide intrusions. Styles of mineralization in the state are primarily copper porphyry, epithermal, and skarn connected with the Laramide orogeny (Ochoa-Landín *et al.*, 2011). The field, located near the eastern edge of the Sonoran Desert at the western margin of Sierra Madre Occidental, is sparsely vegetated by arid scrubs.



Fig 1.: Location of the field of study (the black rectangle)

Multispectral satellite imagery from ETM+ (Landsat 7) and ASTER (Terra) instruments, digital elevation model ASTER GDEM, as well as 1:50 000 geological map published by the Mexican Geological Survey were used in the study. Space-borne imagery was obtained at a time of relatively poor development of vegetation to reduce its influence on rock and ground spectra (March 2003 and February 2006 for ETM+ and ASTER, respectively).

In the research area, there is a known example of a gossan used for analysing its spectral response and comparison with other

objects. It is called Tabisco Gossan, which is a product of weathering of a low sulphidation epithermal gold-silver system. It is dominantly composed of a mixture of Fe oxides and hydroxides (limonite) with clay and other secondary minerals in lesser amounts (Taylor, 2012).

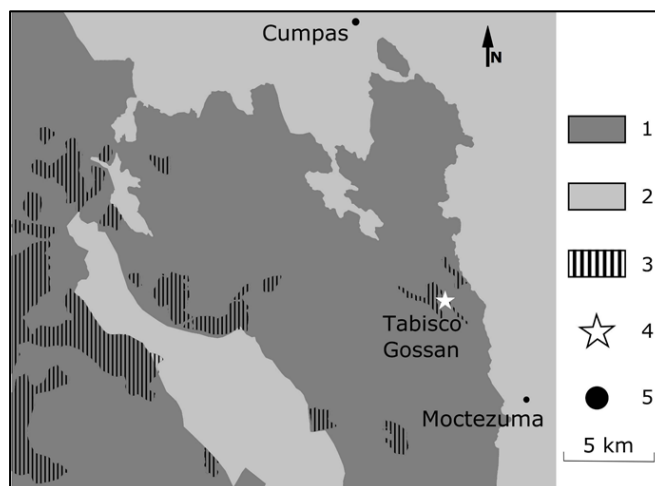


Fig 2.: Schematic geological map of the study area (based on Cumpas H12-D14, Carta Geológico Mexicano, Servicio Geológico Mexicano 2006)

1) late-Cretaceous - Miocene volcano-sedimentary rocks, 2) Pliocene-Holocene sedimentary rocks, 3) alteration zone, 4) test field gossan, 5) town

The analysis of the satellite imagery included colour composites, band ratios, and other methods visually enhanced with image processing operations. Additionally, the detection of the lineaments, as well as assessment of their geological significance, was performed by means of visual interpretation and image enhancement techniques on satellite imagery and DEM. With the unsupervised ISODATA classification of ETM+ data, classification maps have been produced. Their groundtruthing was done with the geological map and tested with the use of statistical methods.

The methods applied revealed occurrence of areas with high ferric oxide content connected with alteration zones, which probably are closely related to gossans.

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## Investigation of rock clasts collected by dredging of mega-blocks in the Central Barents Sea

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During cruise HH-12 rock samples were collected by dredging. The main objective of the dredging was investigation of mega blocks in the central part of the Barents Sea. Samples were analysed by lithological and petrophysical methods.

The main investigation methods were macro description, which was carried out onboard. With this method, the main rocks characteristics, such as color, structure and texture were described. Another method, a more detailed micro description was carried out also. It was performed in the university after the thin sections were prepared. Using this method permits exactly to define the composition of the rocks, evaluate the percent volume of the components and give characterization of the grains. Resolution of the method is 0.2 mm. The last used method was X-ray computer tomography (CT), which is a non-destructive technique. It reveals the internal structure of objects, determined by variations in density and atomic composition. Large number of parallel 2D sections can be obtained, which allows 3D imaging of selected features. Also this technique allows calculating porosity and fluid flow characterizations. The resolution of that method is about 1 µm. This method was carried out on sandstones with zircon content. The zircon was separated, than analysed. Due to the grain morphotype of the zircon (Pupin, 1980, Belusova *et al.*, 2006), we supposed the genesis of the sandstone blocks.

The dredge was taken to collect samples of the rocks, which form the ice-rafted mega blocks mapped in the Bjornoyrenna (Fig.1).

The main material which was collected during dredging was sandstone. Nearly 80% of all selected rocks were sandstone clasts. The composition of sandstones based on the micro description is pretty same. The volume of quartz grains vary between 60 and 80%, feldspar ~10-30% and rock fragments ~5-15%. One of three studied

samples had a special feature: heavy minerals occurred in parallel structures in the rock.

Besides sandstones, a dolostone sample was also investigated. From CT data, some low x-ray density patches were found, which can be clay or organic material, but it is difficult to say what exactly it is. This unknown phase forms also parallel structures in the rock. Silty-sandy claystone was also analysed. The main features of this sample were the abundant fractures, which were filled with different material, such as heavy minerals and calcite. And the last sample was weathering crust, very oxidized and fragile.

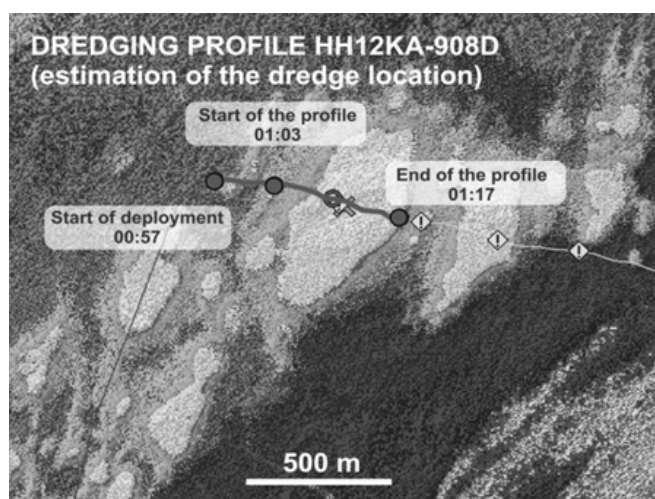


Figure 1. Dredging profile

Belousova E.A., Griffin W.L., O'Reilly S.Y. (2006): *J Petrol*, 47/2: 329–353.  
Pupin J. P. (1980): *Contrib Mineral Petrol*, 73: 207-220.

## Minerals of the Kope Magnetite skarn deposit, Slovenia

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The Kope Mountains are located in the western part of the Pohorje Mountain range, which belongs to a south-eastern part of the Eastern Alps (NE Slovenia). The Pohorje metamorphic complex represents the largest eastern intrusion of granodioritic magma along the Periadriatic Fault, separating the Eastern Alps from the Dinarides. On its north side it borders to the Middle-Miocene Ribnica tectonic basin, on the west and south-west side it is bound to the Labot Fault, whereas to the east and south-east it gradually sinks under the younger sediments of the Pannonian basin.

The polymetallic ore deposit at Kope was formed by contact metamorphism, induced by intrusion of a dacite magma in the northwestern part of the Pohorje Mountain chain (Germovšek, 1954). The intrusion of dacite magma into the carbonate and calc-silicate rocks produced epidote and garnet dominated skarns, richly mineralized with oxide and sulphide ore minerals including magnetite, hematite, pyrrhotite, pyrite, galena, sphalerite, chalcopyrite and minor Ag-, Mo-, W-, Bi- sulphides and tellurides. The ore deposit outcrops in form of small ore-bodies is hosted by skarn rocks, which include garnet, epidote and hedenbergite in various ratios.

The majority of calcareous skarn minerals (Einaudi & Bruk, 1982) show variable chemical composition, often following the crystal growth zones, indicating alternating composition of mineralizing solutions. Garnet compositions are largely dominated by andradite. The growth zones are parallel to the crystallographic faces and their chemical composition varies as their color, from andradite to grossular, almandine, spessartine and their isomorphous mixtures. Epidote group minerals, represented by epidote and clinozoisite, show transitions to piemontite (Mn) and allanite (Ce and La). Epidote crystals include rounded grains of zircon, apatite, rutile and feldspars, while the fractures are filled with quartz or calcite. The next typical skarn mineral group include pyroxenes which are represented by hedenbergite, diopside and pigeonite with compositional changes shifting towards wollastonite (Ca) and ferrosilite (Fe). Calcareous silicates are accompanied by feldspars, orthoclase and plagioclase, and micas (muscovite and biotite). Biotite is often altered to chlorite by younger hydrothermal process and accompanied by idiomorphic titanite crystals.

Magnetite is the main ore mineral of the Kope deposit. It crystallises in form of idiomorphic octahedral crystals together with garnets replacing the primary silicate minerals. It includes amphiboles, apatite, titanite, molybdenite, scheelite, hematite and sulphides. It often fills the pores of fractured skarn minerals, indicating that the hydrothermal event that produced magnetite happened during tectonic activity. Magnetite replacing the silicate minerals commonly shows Si-rich zones. In the final stage of growth, magnetite is associated with idiomorphic quartz crystals. Hematite and ilmenite are less abundant and precede the crystallization of magnetite.

The most common among the sulphide minerals is pyrite. It appears in the form of idiomorphic cubic crystals, sometimes replaced by magnetite. It is followed by chalcopyrite, which often

fills the fractures in pyrite crystals and pyrrhotite that has been attributed to the breakdown of pyrite during metamorphism. Chalcopyrite is accompanied by minor sphalerite and galena. On the onset of oxidation, chalcopyrite alters to bornite and covellite, which further oxidize to hydroxyoxides and hydroxycarbonates. The mineralogy of the oxidation zone comprises goethite, limonite, cerussite, smithsonite, malachite and azurite forming encrustations (Fig. 1) around fractured ore minerals, especially Bi-rich phases.

Bi-rich phases that appear in the Kope skarns are thought to be the product of the last, hydrothermal phase that fills up the pores and fractures in garnet, magnetite and pyrite crystals and mineralizes voids between the primary minerals (Fig. 2). They are represented by native bismuth, bismite, bismutinite, tellurobismuthite, Ag-rich cosalite (Štruel & Kluge, 1991) and tetradymite, in addition to numerous yet unidentified Pb-Bi-S, Ag-Bi-Te-S, Ag-Pb-Bi-S, and Cu-Fe-Bi-S sulfosalts.

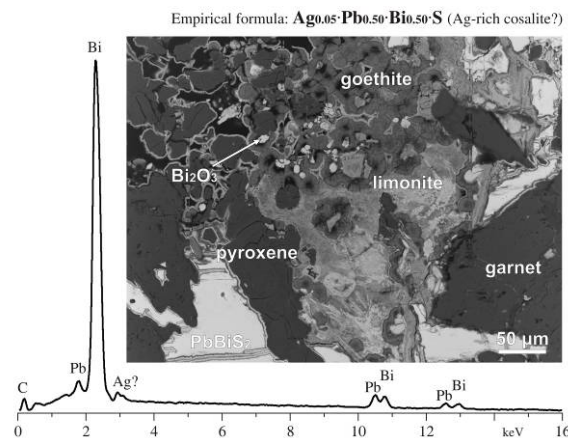


Fig. 1.: Tectonically shattered garnet and pyroxene crystals. The fractures are filled with Bi-rich minerals (Ag-cosalite) and Fe-oxyhydroxydes.

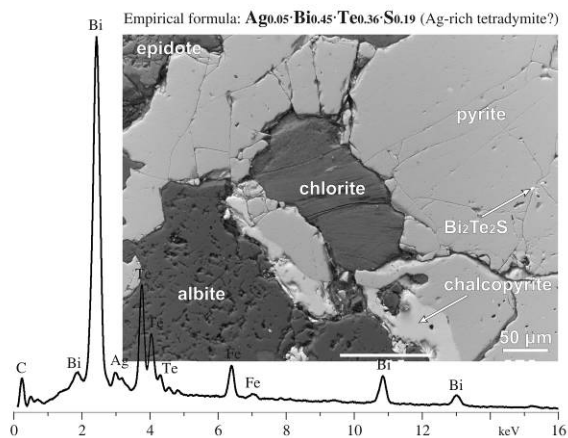


Fig. 2.: Fractured pyrite crystal with albite, epidote, chlorite, chalcopyrite and inclusions of Bi-rich sulfosalts (Ag-tetradymite).

Einaudi, M.T., Brut, M.D (1982): Econ Geol, 77: 745-754.

Germovšek, C. (1954): Geologija, 2: 191-271.

Štruel, I., Kluge, R. (1991): Geologija, 34: 305-335.

## Oil to source rock correlation in Zaláta East-1 well, Hungary

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The Zaláta K (East)-1 exploratory well is located nearby the river Dráva in the administrative area of settlement Piskó, Baranya County, South-West Hungary. Geologically it falls in the area of Drava Basin. The objectives of the drilling were to explore and test hydrocarbon potential of two horizons in Badenian conglomerates on the basis of 3 D seismic interpretations in the Zalata-Dravica East seismic block. Zaláta East-1 well reached a total depth of 3010 m in synrift breccia (Koncz *et al.*, 2010).

Previously drillings (Zaláta-1, Dravica-1) resulted in gas inflow with condensate from dolomitic limestone and breccia reservoir under Middle Miocene sedimentary rocks consisting of sandstones, siltstones and silty marls. But the new well (Zaláta East-1) resulted in heavy oil sample. The API gravity of the crude oil sample from the Zaláta East-1 well is 28.2 and it has intermediate character based on the first key fraction.

Based on the screening analyses (1850 to 2665m) performed on cuttings source rock bodies were identified in Szolnok Formation and Endrőd Formation to Badenian sections.

The questions are as follows: What sources have generated hydrocarbons? What grade of thermal maturity characterises the generating sources?

To answer the questions source rocks from mentioned formation and crude oils were studied using several geochemical techniques (GC, GC-MS, EA-IR-MS).

The GC analysis of light hydrocarbon fraction from crude oil shows low thermal maturity using Thompson category (IHP=0.65), while the aromaticity ratio (toluene/n-heptane) refers slightly water washing. The whole oil chromatogram is showing a lack of biodegradation and slightly reductive environment of source rock based on pristane-phytane ratio (Pr/Ph=1.24) (Peters *et al.*, 2005).

According to our earlier results the Lower Pannonian and Miocene source rocks are genetically different from each other in samples studied from Zaláta East-1 well.

The Lower Pannonian samples have not or have very low amount of oleanane showing minor terrestrial input to biomass based on mz191 fragmentogram. The sources in Lower Pannonian sequence have high hopane-sterane ratios (>7.5). Based on isotope composition of saturated and aromatic fractions separated from rock extract of Miocene sample are isotopically heavier than Lower Pannonian ones.

Investigating geochemical data from oil fractions we can get a good correlation with Miocene source rocks. The oil sample has oleanane, what is a constituent part of oils derived from Miocene sources in other parts of Hungary. Analogy can be seen in the mass chromatograms of m/z=218 as well (Fig. 1.). Both oils and Miocene sources have low hopane-sterane ratio approving genetic correlation. According to isotope ratios of crude oil is genetically similar from that of Miocene rock.

Based on biomarker data we can conclude that Lower Pannonian extracts from Szolnok formation do not or barely reach the equilibrium values showing their immaturity.

The thermal maturity parameters indicate that oil can be considered as autochthonous (indigenous) having no considerable vertical component of migration and its maturity corresponds to early oil-window.

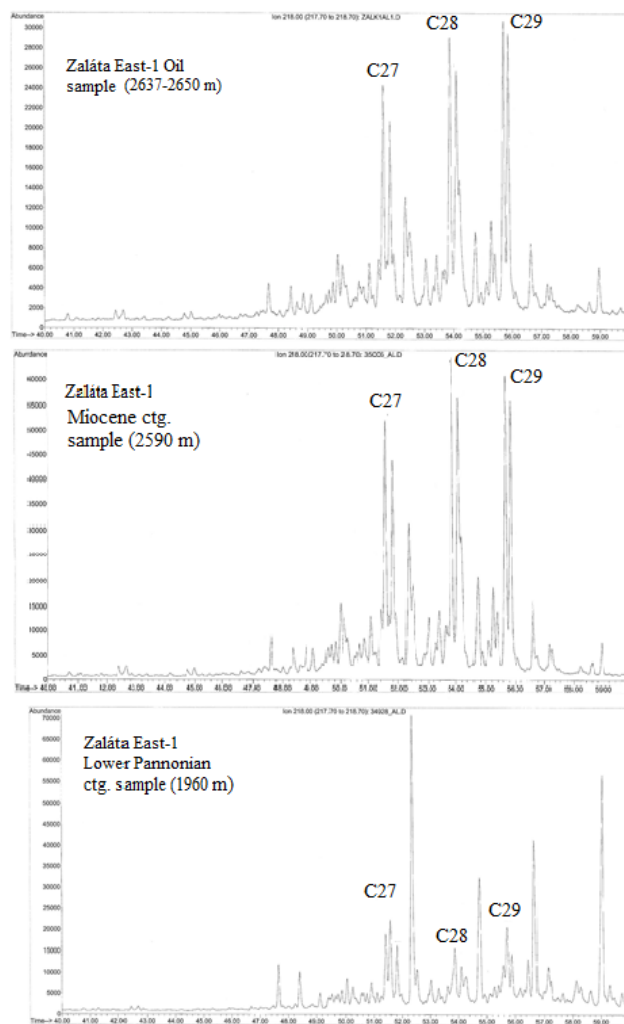


Fig. 1.: Representative mass chromatograms (m/z=218) of rocks and oil

Koncz, I., Lukács, T., Horváth, Zs., Gellért, B., Kajári, M., Lilit, C., Marica, B., Dijana, B. (2010): Organic facies of Lower Pannonian and Middle Miocene sources in northern flank of Drava Basin, The Annual Meeting for the Geoscientists, Szeged

Peters, K. E., Walters, C. C., Moldowan, J. M. (2005): The biomarker guide I-II, 2<sup>nd</sup> ed.: Cambridge, UK, Cambridge University Press



## Changes of pH and EC in alkaline sediments in the context of water content, southern Hungary

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The salinization is one of the most important terraforming processes and its research has long history in Hungary (Abrol *et al.*, 1988; Kádár, 1995; Szendrei, 2006; Tóth, 2005). The natural ancient alkaline areas are in danger, because of the water management in the 19<sup>th</sup> century, and the agriculture and climatic change (Boros, 1999; 2010). These areas have an individual ecosystem, which is very sensitive to environmental changes (Zhang *et al.*, 2013). It is important to know all the geochemical processes which are forming the typical landscape of these areas because of the more effective protection.

Our aim was to define the changing of pH (active and potential acidity) and the EC in the sediments of the Lake Fehér near Kardoskút, Southern Hungary (Fig. 1). Two sampling dates were chosen to analyse the changing of these two parameters. The sampling dates were designated on the basis of the water content of the sediments. The first sampling time was in the summer of 2012 and the second one was in the autumn of the same year.

The study area was designated representatively. We have chosen a typical alkaline area on the shore of the Lake Fehér of Kardoskút. It has high evaporation rate and saline efflorescence appears in the summer.

We investigated the water content, the particle size, the pH and the EC of the alkaline sediments. Two drill cores were taken; one in the summer and one in the autumn of 2012 and each was 1m deep. The cores were analysed with 5cm resolution.

The upper 25-30 cm of the sediment of Lake Fehér has intensively changed during the year. The whole drill core consists of coarse silt. The top of the lake sediment totally dries out to midsummer and the soluble substances leave with the capillary upflow water and appear on the ground as saline efflorescence. The hiatus of the salts of alkaline hydrolysis in the upper 25-30 cm of the sediment is supported by the pH and EC values. This trend which exists during the dry months changes after the autumn rainfalls. The intensive precipitation takes the precipitated salts to solution and washes them back into the sediment.

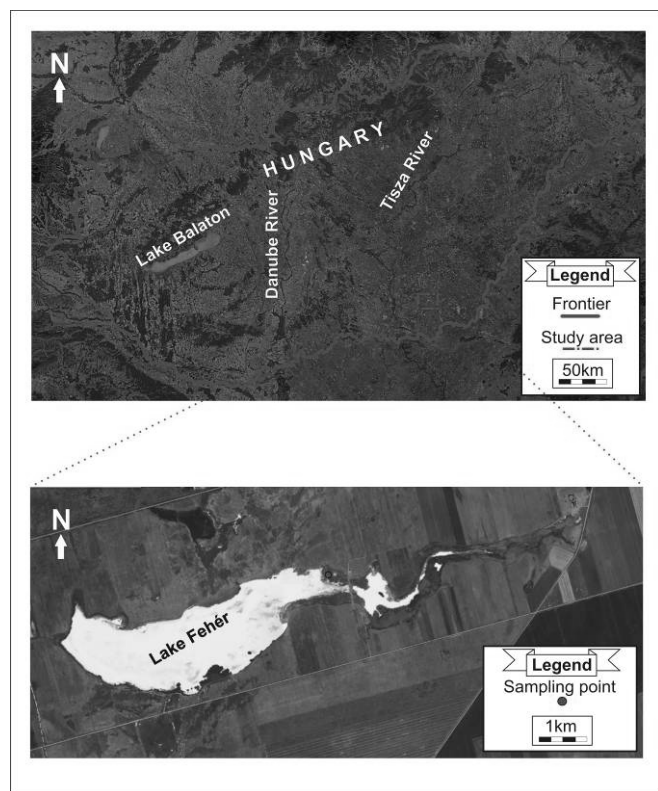


Fig. 1.: The study area

Abrol, I.P., Yadav, J.S.P., Massoud, F.i. (eds.) (1988): FAO Soils Bulletin, 39, pp. 154

Boros, E. (1999): Acta Biol Debr Oecol Hun., 9: 13–80.

Boros, E. (2010): MHT XXVIII. Országos Vándorgyűlés Kiadványa, Sopron: 7

Kádár, I. (1995): A talaj-növény-állat-ember tápláléklánc szennyeződése kémiai elemekkel Magyarországon. Környezet- és természetvédelmi kutatások. A Környezetvédelmi és Területfejlesztési Minisztérium és az MTA Talajtani és Agrokémiai Kutatóintézete kiadványa, Budapest, pp. 388

Szendrei, G. (2006): Topogr Mineral Hung, IX: 21-32.

Tóth, T. (2005): Int Salinity Forum Abs Book: 449-452.

Zhang, L.; Fang, J.; Joeckel, R.M. (2013): Chem Geol, 356: 171-180.

## Petrogenesis and Geochemical Signature of A-type Granite from selected intrusions, Eastern Desert, Egypt

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The Pan-African Orogeny in the Arabian-Nubian Shield was terminated by the intrusion of A-type granites (~595 Ma; Greenberg, 1981) and its volcanic equivalents. Subsequent to the intrusions of these granitic bodies, the shield was exhumed. Eroded A-type granitic pebbles were found in the molasse sediments that were deposited in intermountain basins. Therefore the A-type granites provide information about the last stage of the Pan-African geochemical system. These younger granites are common throughout the Precambrian terrain of Egypt and they played a significant role in the evolution of the Pan-African crust. The whole-rock geochemical data of two granitic intrusions (*G. Um Taghir El Tahtani* and *G. Ras Abda*) from the Central Eastern Desert of Egypt indicate that both of them are subaluminous with A-type characteristics. These intrusions show low CaO content (average 0.61 %wt), high  $\text{FeO}_T/\text{MgO}$  and Ga/Al ratios, and high  $\text{Na}_2\text{O}+\text{K}_2\text{O}$  (average 8.91 %wt). The A-type granite of the two plutons are marked with enrichment of high field strength elements content (Zr, Nb, Y and Ga) and depletion in MgO (0.05-0.58 %wt) and with low concentration of Sr and Ba. The studied granitoids were intruded within a plate extensional regime.

Greenberg, J.K. (1981): Bull Geol Soc Am, Part 1., 92: 224-232.



## Different hydraulic position of paleo-maar lakes in subsurface flow systems, Tihany Peninsula, Hungary

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Groundwater-influenced lakes and wetlands are hydrologically and ecologically linked to adjacent groundwater bodies, but the degree of their interactions is highly variable in space and time (Born *et al.*, 1979, Winter *et al.*, 1998). The relationship depends on the water table configuration, location of stagnation points, relation of the lake water level to the water table and to the subsurface potential field, the geological framework, climate, and the vegetation (Winter 1976, Winter *et al.*, 1998).

The lakes of Tihany Peninsula, Hungary are located in Neogene paleo-maar structures filled with lake sediments (Németh *et al.*, 2001). The lakes were assumed to be recharged exclusively from precipitation. However, based on the above mentioned considerations, and on the numerical and theoretical studies of Winter (1976), connection of the lakes with the groundwater can be presumed. The goals of the study were to understand the hydraulic position of these lakes in the flow systems of the Peninsula and to find explanations for their different hydrological behaviour.

Cadastral- and topographic map analysis, radio-magnetotelluric (RMT) measurements, hydraulic-, geochemical methods, time series analysis and two-dimensional numerical flow-simulations (FLONET/TR2; Molson & Frind, 2013) were used to understand the hydraulic position of the lakes (Fig. 1.).

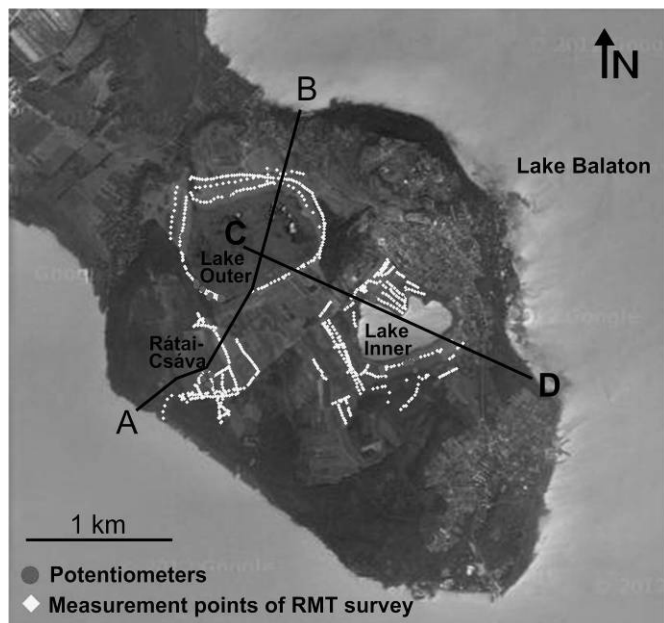


Fig.1.: Points of measurements and location of cross sections used in 2D numerical groundwater flow simulation

As a result, a hydraulically continuous subsurface flow field was recognised for the area, which is driven by topographic gradients. The geometry and hydraulic behaviour of the near-surface sediments was described with the help of the geophysical (RMT) measurements. Seasonal variability of the subsurface fluid potential field and the groundwater-chemistry was revealed by the hydraulic

and hydrogeochemical field data analyses. Based on this insight, a two-dimensional numerical simulation was carried out. The model indicated the different hydraulic position of the lakes. The transient lake (Ráta-Csáva) is a recharge type lake, the basin of the Outer Lake is a discharge area, however the Inner Lake is a through-flow type lake (Fig. 2.). The results are in good agreement with the field measurements.

As a conclusion, the paleo-maar lakes of the Tihany Peninsula are part of the water level, therefore the subsurface hydraulic connection between the lakes has been recognised. The different hydraulic behaviour of the lakes is strongly depending on their subsurface flow position.

These results can be significant concerning water balance and ecological aspects of the wetlands as well as in the management of the conservation of the area. These results can also initiate further research to understand the interaction between flow systems and paleo-maar lakes for other regions.

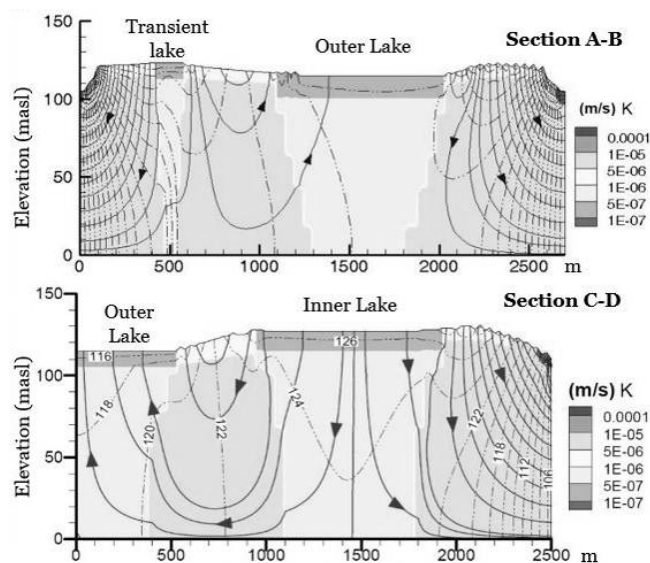


Fig.2.: The potential distribution and streamlines along the simulated sections by FLOWNET TR2

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# Petrographic analysis of Gyűrűfű Rhyolite Formation using the thin section collection of MecsekOre Company

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In this study the samples of the „Vulkanitok, etalon kollekció” thin section collection (MecsekOre Ltd.) were examined, representing the Permian Gyűrűfű Rhyolite Formation (selected boreholes and outcrops, W Mecsek Mts.; core Bisse-1, northern foreland of Villány Mts.) and Cserdi Conglomerate Formation (boreholes and outcrops, W Mecsek Mts.).

The Permian Gyűrűfű Rhyolite and Cserdi Conglomerate Formations occurs in the Mecsek Mts and surrounding areas – within South-Transdanubian Unit –, where during the Variscan orogen cycle formed basin sedimented in thick molass layers. The Gyűrűfű Rhyolite Formation in the W-Mecsek was documented like rhyolitic rock “quartzphorphyr”, which subordinated set between the bedrock (Korpádi Sandstone) and the covering (Cserdi Conglomerate) Formations (Fazekas, 1978; Fülöp, 1994; Barabás & Barabásné Stuhl, 1998).

In this study the used samples are from by Via Fazekas assembled etalon thin section collection. During the reambulation we observed special marks which help to microscopically distinguish the old, transformed volcanic rocks from the magmatic explosive and pyroclast flow origin rocks (McPhie *et al.*, 1993; Paulick & Breitkreuz, 2005).

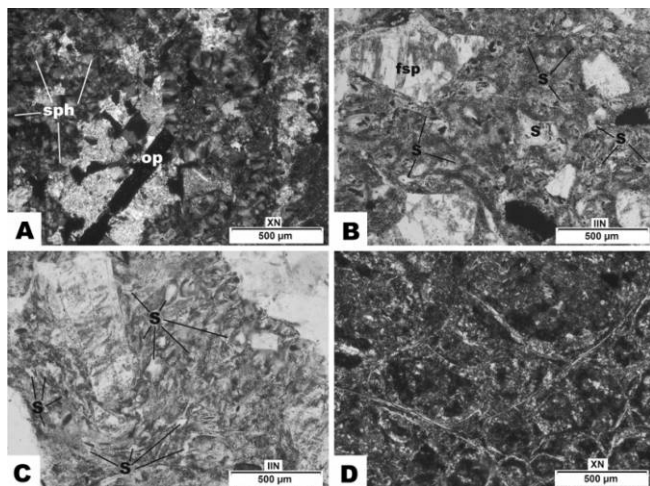


Fig-1: A) Spherulites (S) and opac pseudomorphs (op) in devitrified pumice B) Matrix with abundant feldspar crystal fragments (fsp) and devitrified glass shards C) Glass shard-rich (S) relict vitroclastic textures D) Relict perlitic structure

In the descriptions about the Gyűrűfű Rhyolites were determined like quartzphorphyr with microcrystal felsitic texture. Supposedly, that the groundmass was once glassy and silicified. In the felsitic matrix it could appear as a flowing structure which was identified by tear or lobe shaped forms (Fazekas, 1978; Barabás & Barabásné Stuhl, 1998).

In my observation these structures are relict pumices and glass shards (Fig. 1/B). The strongly transformed, discontinuous, interrupted patterns are typical vitroclastic marks in pyroclastics. The relict glass shards, which once formed the volcanic glass, had

changed (recrystallization, silicification and argillitization). The shape of the relict pumices and glass shards depend on the volume of the welding. The evidence of the welding, high-temperature devitrification and compaction are the emergence of the spherulitic-axiolitic patterns and the deformed, elongated-flattened frequent appearance of glass shards. Build of potassium feldspar spherulites generally appear in the middle of the pumices and shards while the axiolites occur in the margins (Fig. 1/A). Inside the pumices microquartz or mosaic macroquartz were crystallised. Based on the abundant appearance of broken, splintery phenocrysts and microphenocrysts probably they are magmatic explosive, pyroclastic flow origin rocks. The texture of the Gyűrűfű Rhyolite samples are mainly recrystallised, porphyritic and the groundmass are relict vitroclastic.

The Cserdi Conglomerate samples contain framework volcanic rock fragments with felsitic and pumice origin altered relict vitrophyritic-vitroclastic textures. The texture of the relict vitroclastic grains (Fig. 1/C) is highly similar to the characteristic patterns of the rocks of the Gyűrűfű Rhyolite Formation, however the felsic grains do not occur in the samples from W-Mecsek. The relict vitroclastic clasts are abundant in spherulitic and axiolitic pumices or pumice fragments/shards. The shards usually have blade-like shape, but typical are the cusate or platy shapes as well (Fig. 1/C). Characteristic patterns are the „tubes” in pumices which are the former space of migrating volatiles.

Volcanic texture of the specimens from the core Bisse-1 can be classified as altered homogenous porphyritic perlitic one where the groundmass is devitrified (Fig. 1/D). The devitrification could take place under low-temperature and the former glass transformed to phyllosilicates and quartz. It can develop both in flow rhyolites and pyroclastics (McPhie *et al.*, 1993; Szepesi, 2007).

My results confirm the hypothesis that the rocks of the Gyűrűfű Rhyolite are at least partially derived from magmatic explosive pyroclastic flows. Probably when the Cserdi Formation started to accumulate, this process did not stop, but volcanosediment layers were contemporarily deposited.

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The author would like to express his gratitude to Varga A. for the supports and constructive reviews during the work. Also thanks to the MecsekOre Ltd. for providing me their collection.

## New geochemical data, further supporting hydrothermal contribution to the formation of the Úrkút Mn-ore, Hungary

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At the mining area near Úrkút mineral exploitation has been going on from 1925, although production is continuously declining in the last decades because of the diminishing market demand.

The Úrkút deposit is located in the Bakony Mountains, in the Transdanubian Central Range zone. The geologic framework of the deposit is determined by the surrounding Triassic platform carbonates. Both the formation environment, the size and the depth of the deposit is controlled by fault systems in these carbonates. Plastic deformation also played a significant role in the structural evolution of the mountains. In the middle Jurassic rifting of the carbonate platform resulted in uneven bottom topography that limited the oceanic circulation and led to the development of anoxic conditions. The accumulation of manganese is strongly connected to this Toarcian Oceanic Anoxic Event. The fluctuation of the redox boundary was a necessary factor in the precipitation of manganese minerals. According to  $\delta^{13}\text{C}$  isotope values, Mn-carbonate ore was formed from a precursor Mn-oxide ore during diagenesis (Polgári *et al.*, 1991).

This deposit is a black shale-hosted Mn-carbonate ore. Its areal extension is ca. 10 km<sup>2</sup>. The thickness of the whole black shale sequence is about 40 m which hosts the maximum 10-12 m thick Main Ore Bed and the thin Ore Bed II.

The ore itself comprises alternating clay marl - carbonate marl laminae. It consists of micritic carbonates (mainly rodochrosite), clay minerals (celadonite), goethite and small amounts of quartz and apatite.

The underground mine at Úrkút is one of our important prospects in the ongoing Critical Elements project at the University of Miskolc, Hungary. In this study we provide new data on the elemental composition of the Úrkút carbonatic manganese ore and the associated formations.

Up to date, we have received the chemical data of 59 samples. 31 samples are Mn-carbonate ore, 10 of them are black shale, 8 of them are manganese clay, 4 of them are underlying limestone, 3 of them are Eplény Limestone, 2 of them are Cservár Flintstone and one sample is an oxidic manganese nodule.

The data of the Mn-carbonate ores show that the different colour-types of these ores have different chemical and mineralogical composition.

The total rare earth elements (REE) concentration is on the average 1.4 times the Clark value ( $\Sigma\text{REE}$ : 266 ppm). The Post Archaean Australian Shale (PAAS, thought to represent upper continental average concentration) normalized REE-diagram (Fig. 1.) shows that all Mn-carbonate ore samples show positive

Ce-anomaly. This anomaly is probably due to the anoxic conditions prevailing during sedimentation and diagenesis. We found 3 brown banded Mn-carbonate ore samples that have strong positive Eu-anomaly. This, together with the high Ba-concentration may refer to more intensive hydrothermal contribution in this type.

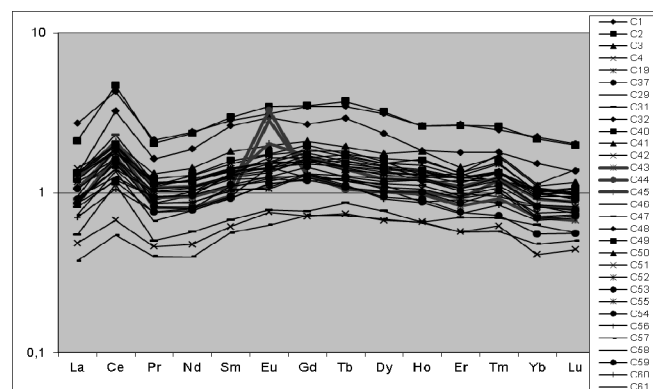


Figure 1. The PAAS normalized diagram of the Mn-carbonate ores

Co is present in relatively high concentrations. According to SEM investigations (Polgári *et al.*, 2000) Co appears in small sulfide mineral grains (cattierite, Co-Ni- and Co-Ni-Fe-sulfides). Its concentration is between 71 and 2601 ppm, averaging 330 ppm that equals 28 times the clark value (if we do not count with the outstanding 2601 ppm value, the deviation is 175 ppm). The highest concentration of Co is found in the reddish brown ore.

Our final goal is to give additional value to the existing manganese ore with the help of gaining knowledge from the rare elements in it. With an appropriate hydrometallurgic method we can extract REEs and Co as a byproduct from Mn-carbonate ores.

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This work was carried out as part of the TÁMOP-4.2.2.A-11/1/KONV-2012-0005 project as a work of Center of Excellence of Sustainable Resource Management, in the framework of the New Széchenyi Plan. The realization of this project is supported by the European Union, cofinanced by the European Social Fund.

## New geochemical data of the Mecsek Hard Coal Formation

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Critical raw materials are essential for the efficient functioning of Europe's economy. The Miskolc University manages the EU supported project (CRITICEL – [www.kritikuselemek.uni-miskolc.hu](http://www.kritikuselemek.uni-miskolc.hu)) to carry out research in relation to critical raw materials in Hungary.

Coal may be enriched in certain trace elements (B, Be, Ge, Mo, U, V) because of the absorption capacity of organic matter that is why the geochemistry of coal is an important exploration target.

The Eastern-Mecsek Mts. (SW-Hungary) contains important hard coal deposits, with identified resources of about 1 billion tonnes. The Mecsek Hard Coal Formation was deposited during the Late Triassic - Early Jurassic (Hettangian, Early-Sinemurian) in a half-graben sloping towards south, with coal seams becoming thicker towards the south (Nagy, 1969). Historic assays indicate high trace metal (Be, Ga, Ge, Li, Mo, Nb, Pb, Sn, Ta, Tl, Zr) concentrations.

The source of the abovementioned elements in the coal may be linked to the neighbouring exposed granitic and metamorphic rocks formed in the Carboniferous and the alkaline basalt sills (and fonolite intrusives) formed in the Cretaceous.

Our aim is to collect geochemical data by using modern analytical techniques (ICP-OES, AAS, XRF, RTG, SEM) to reveal the concentration of the trace elements, compare the analysed areas and give a genetic model for the origin of these elements.

The samples were collected from three areas of the Mecsek Mts.: Pécsszabolcs (17 composite samples from 97 core sample), Pécs-Vasas (16 samples) and Nagymányok (8 samples). ICP investigation was carried out by ALS Global and MFGI for 64 elements. Samples are represented by coal, natural coke, alkaline basalt and metabasalt, tuffite, marl and siliciclastic rocks such as sandstone and claystone.

The geochemical data show high average niobium (142 ppm) and tantalum (10 ppm) concentrations in the Pécsszabolcs area, where these elements are enriched 30-35 times compared to the average Earth crust concentration. In the Pécs-Vasas area, these concentrations are lower, the Nb and Ta contents are 6-8 times that of the average Earth crust concentration. Furthermore the average zirconium concentration is about 444 ppm at Pécsszabolcs (it means 12.34 times higher values, than the average Earth crust), but at

Pécs-Vasas this concentration is also lower (average 145 ppm – 4 times higher values than the average Earth crust) (Seredin & Finkelman, 2008). Hafnium also shows enrichment in these samples. At Pécsszabolcs 11.8 times higher than the average Earth crust (13.8 ppm), in opposite to Pécs-Vasas where these values are 3 ppm which means 2.5 times enrichment compared to the average Earth crust.

There are some differences between the correlation coefficient of Nb and Ta in the Pécsszabolcs (0.95) area compared to Pécs-Vasas (0.89).

The Rare Earth Element (REE) assays also show differences between the abovementioned two areas. At Pécsszabolcs the  $\Sigma$ RFF is 332.44 ppm in average, while at Pécs-Vasas this value is 166.93 ppm.

The Nb, Ta, Hf, Zr and REE enrichment in the coal assemblage shows a 'primary' (or older) effect of the weathering of the Carboniferous granite and a secondary alkaline magmatic overprint during the Cretaceous. The primary effect might be stronger on the northern area due to paleogeographical conditions, while the latest secondary overprint might be even more effective in the Pécsszabolcs area.

Our aim is to reveal the enriched phases by XRF, RTG and SEM to separate the phases responsible for the enrichment and reveal the origin of these elements.

Nagy, E. (1969): Bull Hung Geol Inst, 51/2: 289–319.

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This work was carried out as part of the TÁMOP-4.2.2.A-11/1/KONV -2012-0005 project as a work of Center of Excellence of Sustainable Resource Management, in the framework of the New Széchenyi Plan. The realization of this project is supported by the European Union, cofinanced by the European Social Fund. This work is supported by the Wildhorse UCG Ltd., the Pannonpower Ltd. and the Calamites Ltd. The samples were analysed by ALS-Global and MFGI.

## Strain and deformation measurements in rock massive using borehole geophysics

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Borehole geophysical surveys are carried out to determine the distribution of a certain parameter in depth. Combining different measurements of different parameters and their correlations, it is possible to make conclusions about the geology, borehole technical condition and etc. In this paper the authors are showing the applications of the Acoustic Borehole televiewer – BHTV. The BHTV probe uses fixed acoustic transducer and a rotating acoustic mirror to scan the borehole walls with a focused ultrasound beam. The amplitude and travel time of the reflected acoustic signal are recorded simultaneously as separate image logs. The method is used for structural interpretation with dip and dip direction, fracture frequency, lithology, casing inspections and etc. The BHTV probe can be used in fluid filled holes ONLY. The BHTV results in generating an unrolled 360 degree false colour image of the borehole wall. The images are orientated to magnetic north in vertical boreholes or high side in the inclined holes using the integrated orientation module.

As it was pointed out before, the instrument produces two separate logs – amplitude and travel time. The travel time is the time that takes the signal to reach and reflect off the walls of the borehole. After making some calculations and determining the ACOUSTIC VELOCITY of the fluid in the borehole, we can determine the distance  $S$  between the tool long axis and the rock wall. The distance is calculated via:

$$S = \text{Acoustic velocity} \times \text{Travel time}$$

The end result is a table with lengths every  $2^\circ$  of circular cross section. This helps us to create a 3D module (Fig. 1.).

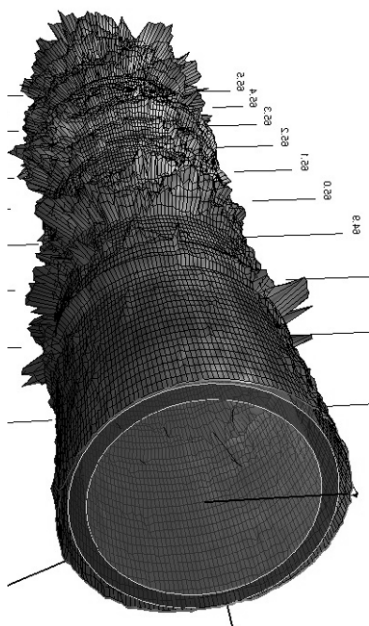


Fig. 1.: 3D borehole model using time travel data.

From the model we are able to create an orientated cross section for every centimetre in depth.

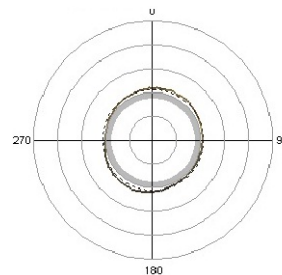
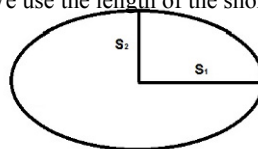


Fig. 2.. An example of a cross section created using the 3D borehole model

On the cross section we can clearly see the strain ellipse (Fig. 2.). The strain ellipse is a way to represent strain in 2D. It is the product of a finite strain applied to a circle of unit radius. The drilling rods have perfect circular cross section, which leads us to believe that the ellipse is the result of deformation after removing the rods. It is an ellipse whose radius is proportional to the stretch  $S$  in any direction. We use the length of the short and long axis  $S_1$  and  $S_2$ .



The ratio  $R_s = S_1 / S_2$  is called the strain ratio and is a measure of the overall intensity of distortion.

The multiplication  $S_1 \times S_2$  is a measure of the area of the strain ellipse. It is used to measure the dilation according to the following formula:

$$1 + \Delta = S_1 \times S_2.$$

Dilation  $\Delta$  is positive if the area increases, negative if it decreases.

Because the instrument has an inbuilt orientation module, which uses magnetic inclination and azimuth measurements, we can orient the ellipse in space and also in depth and so orient the direction of the stress.

If we measure the stress distribution over time in a borehole / boreholes located near an open pit mine, for example, we can see how much has the stress changed in size and direction, due to the removal of great amounts of material. Doing so, we can calculate the rotational component of deformation using the orientation of the strain axis before  $\phi$  and after some time  $\phi'$ . The difference

$$\omega = \phi' - \phi$$

is a measure of how much overall rotation has occurred during the excavation in the mine.

This technique can be implemented in underground mine activities to trace the rock massive stress changes in depth as the tunnelling work progress, helping to prevent accidents. It can be used to monitor the effect of “heavy” buildings on the substrata.

It can be used to create three dimensional models of the stress strength, direction and change in time and in depth. Such models can be used to monitor open and underground mines, seismically active faults and different zones of interest.

## Regional hydro geological characteristics of complex neogen aquifer Mizian hydrogeological region (Mizian plate)

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The territory of the Mizian platform was formed aquifers and complexes with Quaternary, Neogene, Cretaceous and Jurassic age. According to the European Water Framework Directive in the Mizian platform region was separated 35 underground water bodies.

Subject of discussion in this article are underground water bodies of Neogene age. They are formed in the following lithostratigraphic units (Fig. 1.):

- Karst waters in Ruse formation BG1G0000K1b041 - presents loess, alluvial deposits and Pliocene clay, sand and limestone.
- Karst waters in Razgrad formation BG1G000K1HB050 - are represented by clay marl, marl, clayey calcareous marl with layers of sandstone to sandstone with layers of marl, limestone slab, in many places with greensand and flint cores.

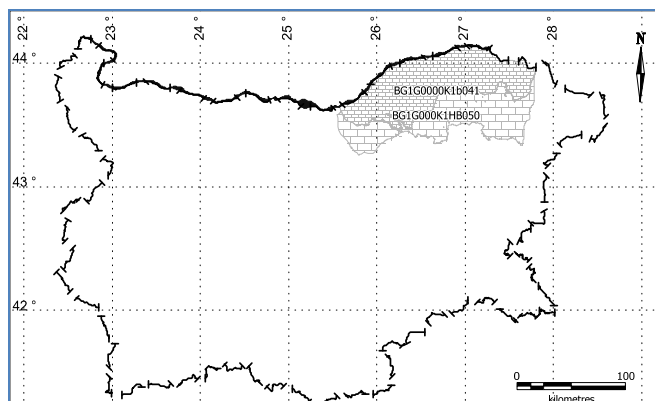


Fig. 1.: Karst waters in Ruse and Razgrad formation

Groundwater bodies under review coincide with lithostratigraphical structures formed during the geological development of the platform area, formed through the same stages of basin sedimentation in similar environments shallow marine and rifts.

Considered groundwater bodies are spatially dependent complexes of alternating Rift limestone, organogenic limestone and marl. The change of sedimentation environment in the course of geological development shallow marine basin during Cretaceous period was the reason for the separation of two lithostratigraphical structures - Ruse and Razgrad suites.

The last has the same geological age, but different lithological composition due to shallowing and frustrating at the bottom of the pool as a result of tectonic movements.

Ruse Formation was formed fracture-karst in karst type, in character-unconfined groundwater. Their movement is carried out by individual watercourses to lower waterbed, which still serve a clay or solid carbonaceous sediment at the base of the complex (the notional boundary between Razgrad and Ruse Formation). Their

direction to the hydrographic grid, but generally the northwest, north and northeast. They are fed by infiltration of rainfall and quaternary (in loess) waters.

In intensive cracking and impressive karst calcareous sediments of the Ruse suite groundwater formed common unconfined, karst aquifer representing powerful radial diverging flow with a general direction of travel from south to north, northwest and northeast - towards the River Dunav (Fig. 2.).

Quaternary sediments are widely spread in the watershed of Rusenski Lom Dobrodjanski Dunavski Rivers. They are represented by different genetic types: proluvial, delluvial, colluvial, delapsivni, alluvial and mixed type deposits and various formations aeolian formations.

Groundwater recharge is done by infiltration of rainfall and surface waters (and along the River Dunav - from river water) of Quaternary and Neogene water, and probably results from malmvalanzhinskiya aquifer. The draining is from river ravine system and from River Dunav, from different sources and flow of many pumping stations (shaft and tube wells).

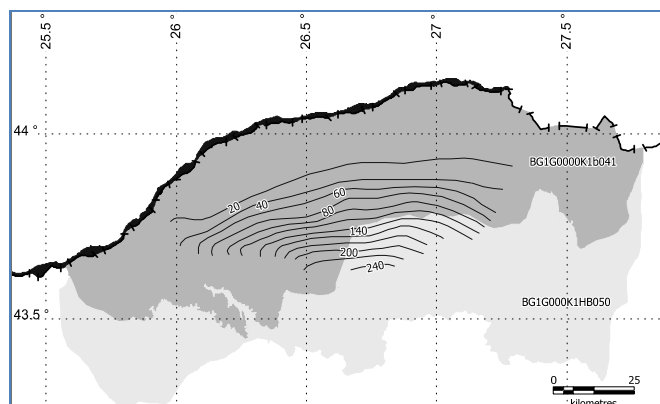


Fig. 2.: The movement of water in both underground water bodies.

The filtration coefficient is ranging 0.03-0.50 m/d to 20 m/d, while a conductivity of 1-2 m<sup>2</sup>/d to 5000 m<sup>2</sup>/d can be observed, but they are advantageously 100-600 m<sup>2</sup>/d with an average of about 450 - 500 m<sup>2</sup>/d. The transmission level is 1.105 m<sup>2</sup>/d to 2.07 m<sup>2</sup>/d, the active porosity characterized water supply is 0.05 to 0.22, and the relative flow rates from single boreholes are from 0.1 l/sm to over 100 l/sm.

General scheme for the use of water in the valleys Rusenski Lom and Dunavski Dobrudjanski reki. Volume II Dunav Region (2000) Bulg Acad Sci

# Paleoecological analysis of regressive, detrital Sarmatian deposits from Borzykowa region (Northern part of the Carpathian Foredeep, central Poland)

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The Carpathian Foredeep is a structure lies between Carpathians and Central-Polish Highlands. It was formed during Miocene when Carpathians finally folded (details in Oszczypko, 2006). This foredeep was flooded by water of Central Parathetys.

Sarmatian deposits cropping out near Chmielnik were deposited in northern part of the Carpathian Foredeep, on varying, older rocks (Radwański, 1973). Miocene rocks are represented here mostly by detrital limestones, sands, gravels, rarely by silts (Rutkowski, 1976). Lithostratigraphically they belong to "detrital Sarmatian" (formerly Chmielnik Fm). These sediments were finally deposited during Early Sarmatian regression and contain mostly redeposited material come from Badenian (e.g. Czapowski & Studencka, 1990).

In the vicinity of Chmielnik, in many exposures, varied fossils of organisms from different marine habitats, though sometimes also terrestrial forms occur. In detrital deposits, marine fossils, typical for average salinity, were found, which are usually interpreted as redeposited fossils, however, euryhaline fossils, typical for water with lower or variable salinity were also recognised, which can be interpreted as in situ fossils. Locally there are a large amount of the terrestrial gastropods (Górka, 2008; Stworzewicz, 2013) and fragments of silicified wood, too.

Large scaled cross bedded quartz sands (clinoforms) in Borzykowa sand pit were analysed. Very fine- and fine-grained sands are dominated, but in some isolated horizons, medium- and coarse-grained sands and gravel occur. The angle of cross bedding measures approximately 15°. Within the cross-bedded sands, numerous, but rarely spaced fossils of small bivalves (usually up to 1 cm) *Macra* (*Sarmatimacra*) *eichwaldi* (Laskarew, 1914) occur. These specimens are usually observed within the deposit in their life position with articulated shells. Furthermore, probably redeposited (disarticulated) bivalves *Solen* sp. were also found there besides small, abraded gastropods and crushed algae. Such allochthonous assemblages mostly occur in horizons of coarse-grained sand and gravels.

Presence of bivalves with articulated shells in life position within the sediment suggest that they are in situ. The small size of bivalves provides that organisms live in unfavorable conditions. Mass occurrence in Miocene deposits such opportunistic forms, with no other organisms is traditionally considered as an evidence of lower

salinity of the Central Parathetys in the Sarmatian (e.g. Czapowski & Studencka, 1990). However in nearest outcrops of detrital Sarmatian (Zwierzyniec, Zrecze Małe, Ślasków), molluscs are much more diverse and larger. Deposition structures in Borzykowa remind sand bars of Gilbert type delta (Gradziński *et al.*, 1986). Such delta could be evidence for the closeness of land and river mouth, what suggest also numerous gastropods and fragments of wood near Zwierzyniec. The Zwierzyniec succession exposes fine-grained, quartz sands with sandy muds. They are horizontally- or very low angle cross-bedded in large scale. Presence of both, euhaline organisms and organisms characteristics for mesohaline waters, suggest, that part of these fossils (euhaline) are redeposited (Stachacz *et al.*, 2013).

Significant lower angle of cross-bedding in Zwierzyniec, suggest lower rate of sediment accumulation than in Borzykowa, furthermore, the same bivalves has bigger sizes. These observations indicate, that the important factor which limit the growth and diversity of organisms from Borzykowa, was high rate of sediment accumulation, not only the lower salinity as previously thought. The lower salinity during Sarmatian is not questioned here, however, Piller & Harzhauser (2005) suggest otherwise possibility. Thus, it is necessary to continue further sedimentological and paleoecological studies on this area and revise the existing views.

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## Sandy-glauconitic horizons in Campanian-Maastrichtian succession in Southern Poland (Miechów Segment) as indicator of sea-level change- preliminary observations

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During Upper Cretaceous Miechów Segment was a marginal part of Polish-Danish Trough, which filling deposits were described “over regional” (eustatic changes) and global events (Subhercynian movement), which affected on sedimentary evolution of neighbouring area (Cracow-Silesia area and Sudetic area). The study of Upper Cretaceous deposits in Miechów Segment is a crucial key in understanding evolution of the whole south Poland and neighbouring area. Sandy-glauconitic horizons in Campanian and Maastrichtian succession of Miechów Segment were noticed by previous authors since 60's (e.g. Rutkowski, 1965) and some of them were called as hardgrounds. In monotonous carbonate (siliceous limestones=opokas with marly intercalations) successions hardgrounds were treated as useful tools in chronostratigraphic correlation in local scale.

Sandy-glauconitic horizons usually indicate decreasing of sedimentation rate or non deposition events, which were usually connected with basin deepening. New interpretations indicate that such horizons can be connected with basin shallowing, rather than deepening. In Hancock (1993) interpretation hardgrounds indicate turn/ or inflection points from LST to HST on eustatic curve for NW Europe.

The main goal of the project was to determine the biostratigraphical position of studied horizons and correlate them with well-known eustatic cycles described in NW Europe.

In Miechów Segment seven sandy-glauconitic horizons were indicated (Fig. 1.). Each of them has different character, which manifest in variable composition of detritic quartz, glauconitic grains and phosphoritic nodules. Different group of fossils (sponge, echinoids, bivalves were also indicated.

Detailed biostratigraphic (based on inoceramid) revision of Campanian and Maastrichtian deposits in Miechów Segment revealed that some of recognized sandy-glauconitic horizons correlate with transgression/regression events determined in isochronous sections in Germany and France (Voigt *et al.*, 2012), England (Jarvis *et al.*, 2002), based on isotope  $\delta^{13}\text{C}$  excursion. Two

recognized horizons did not correlate with event which reflect on eustatic curve, and probably they are an effect of local tectonic movements (probably the Subhercynian phase).

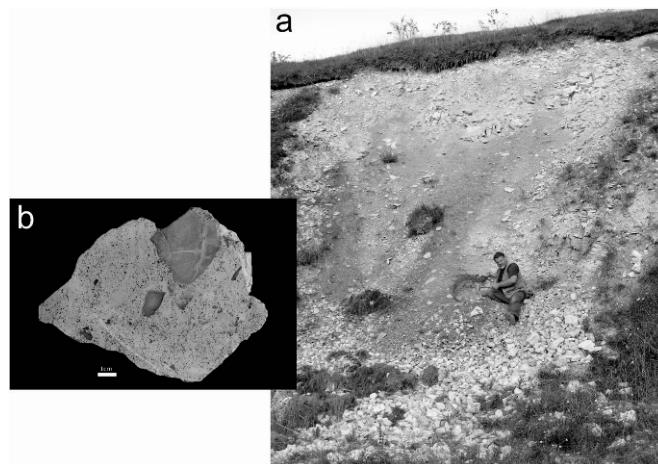


Fig. 1.: Jeżówka outcrop, where a Lower Campanian firmground were described (a) glauconitic clasts on which firmground developed in marly matrix from Jeżówka outcrop.

In the future, more detailed analysis of sandy-glauconitic horizons will be done. Analysis will include palaeontological, petrographical and isotopic ( $\delta^{13}\text{C}$ ) data collection, too. Such interdisciplinary research will help to understand the connection between glauconitic-sandy horizons occurrence and sea level change.

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## The age and stratigraphic position of Stare Bystre Formation (Magura Nappe, Polish Outer Carpathians) based on calcareous nannofossils

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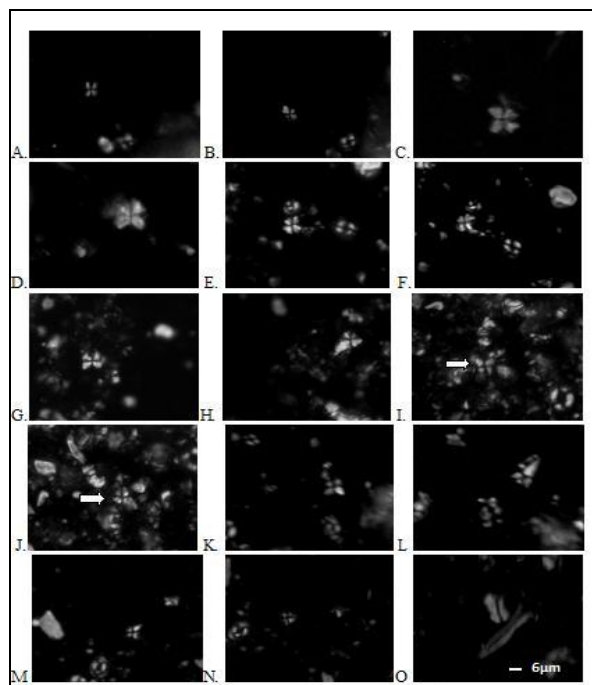
The paper presents biostratigraphic results of studies from Stare Bystre Formation, based on the quantitative calcareous nannofossil analyses. The samples were collected from an outcrop located between Stare Bystre (N49 26.506, E19 55.836) and Rogoźnik, on the left bank of the Rogoźnik Wielki River. The outcrop in Stare Bystre is located in the Orava-Nowy Targ Intramontane Basin which is a part of Krynica zone in the Magura Nappe (Outer Carpathians). In this area marine Miocene deposition emerges to the surface from under the freshwater Neogene and Quaternary lands sediments, which cover the basin area (Cieszkowski, Olszewska 1986, Cieszkowski 1992, Oszczytko 2006). Recently the outcrop has been totally destroyed by mudflows as the results of the expansion of the Rogoźnik River. The samples analysed in the author's master thesis have been collected in 1998 by Marek Cieszkowski and Marta Oszczytko-Clowes. The reason to conduct new investigation in that area was an attempt to clarify the age of the studied formation.

Lithological structure of the Krynica Zone was formalized by Birkenmajer and Oszczytko in 1988/89 who distinguished the youngest deposit in Beskid Group of Magura nappe and proposed the name Malcov Formation. The age of formation was defined as Early Oligocene (Birkenmajer & Oszczytko 1988, 1989, Oszczytko-Clowes, 2001, Oszczytko-Clowes & Żydek, 2012).

In 1992 Cieszkowski discovered marine Miocene deposits in the Orava-Nowy Targ intramontane basin on connection with Magura Nappe series and proposed that the marine Miocene founded in that area could be a continuation of the Malcov Formation and named: Waksmund and Stare Bystre Beds (Oligocene – Early/Middle Miocene age) (Cieszkowski 1992). The age of the Stare Bystre Formation, determined by Cieszkowski based on the presence of: *Reticulofenestra pseudoumbilica*, *Sphenolithus abies* and *Discoaster kugleri* – indicates NN7 (Sarmatian) zone sensu Martini & Worsley (1970).

The age of the sediments discussed in this paper has been defined also based of the calcareous nannoplankton assemblages. Eighteen microscope slides were analysed using the standard smear slide technique for light microscope. The investigation was carried out under Nikon Eclipse E600POL (light microscope), at enlargement of 1000x. 128 species of calcareous nannoplankton have been determined: 16 autochthonous, 112 allochthonous. The early Miocene age (NN2) of Stare Bystre beds have been determined on the basis of first occurrence of *Sphenolithus disbelemnus*. The autochthonous assemblage is characterized by the occurrence of: *Braarudosphaera bigelowii*, *Calcidiscus leptoporus*, *Coronocyclus nitescens*, *Discoaster deflandrei*, *Helicosphaera obliqua*, *Pontosphaera multipora*, *Reticulofenestra dawiesii*, *Reticulofenestra haquii*, *Reticulofenestra minuta*, *Sphenolithus dissimilis*, *Sphenolithus belemnus* and *Sphenolithus moriformis*. The presences of that species also suggest early Miocene age of the Stare Bystre beds.

In all the samples *Sphenolithus abies* or *Discoaster kugleri* were not observed.



Tab.1. Some of the autochthonous species from Stare Bystre Formation (Magura Nappe): A. B. *Sphenolithus dissimilis* (Bukry & Percival, 1971) C. D. and E. F. *Sphenolithus moriformis* (Brönnimann & Stradner, 1960) Bramlette & Wilcoxon (1967) G. H. and I. J. *Sphenolithus* cf. *belemnus* (Bramlette & Wilcoxon, 1967) K. L.M.N. *Sphenolithus disbelemnus* (Fornaciari & Rio, 1996) O. *Zygrhabilitus bijugatus* (Deflandre in: Deflandre & Fert, 1954, Deflandre 1959) and *Semihololithus kerabyi* (Pearch-Nielsen, 1971)

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## Ceramic petrography and Late Bronze Age ceramic material. Case study from Niemczanska site, Wrocław, Poland and reflections on the ceramic petrography condition in Poland

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Niemczańska site is situated in Wrocław, within the north part of the Lower Silesia in Poland. The region contains a number of archaeological sites from different prehistoric and historical periods. Research on the Late Bronze Age Lusatian Culture settlement site on the Niemczanska street have taken place between 2003 and 2005. The site provided rich ceramic material with over 4000 fragments of pottery vessels, few stone artifacts and numerous archaeological objects such as houses, production, storage and waste pits remains (Fig. 1.).

Ceramic analyses consisted of research on its structure, technology of production and purpose of utility. Within set obtained during excavations, several types were designated basing on diversity in elements mentioned above. Majority of the pottery represents “kitchen” or “hard” ceramics with characteristic features of large size vessels and thick walls, used mainly for storage and kitchen purposes. As an example of other ceramic type a “thin” pottery appeared.



Fig. 1.: Pottery fragments in the pit during the excavations in 2003 (Photo taken by J. Baron)

Further phase of research was based on the microstructure analysis taken under the microscope in transmitted and reflected light. During the laboratory research the aim was to analyse the mineral composition of admixture and to examine the microstructure in comparison to the macrostructure (form) of the pottery. 17 thin sections were taken under study presenting a chosen sample from the whole set. During my presentation I am going to present results of the microscope analyses drawing special attention to the relation of the admixture and microstructure with a macrostructure. Petrographic examination has shown the mineral composition of both types of the ceramics. As “basic” elements appearing in most of the samples quartz, plagioclase and microcline grains should be mentioned. Interesting fact observed was domination of stone (mostly granitoids and sandstone) as well as old ceramic fragments in “hard” ceramic, and the fact that grains of big size seem not to be connected with any particular type of ceramic. Exact differentiation in a grain size is going to be presented on the poster. Varied

occurrence of rounded and angular grains also proves miscellaneous admixture sources deriving from both random and previously prepared breakstone.

Directional texture appeared in few of the samples (e.g. NIEM/05/199/a sample, presented on the Fig. 2.) what led to conclusion that this vessels have been prepared in a peculiar way which included strong smoothing of the surface.

The poster is also going to focus on the color, type and burning of the clay minerals in a ceramic mass (as well as following conclusions on the temperature of vessel baking).

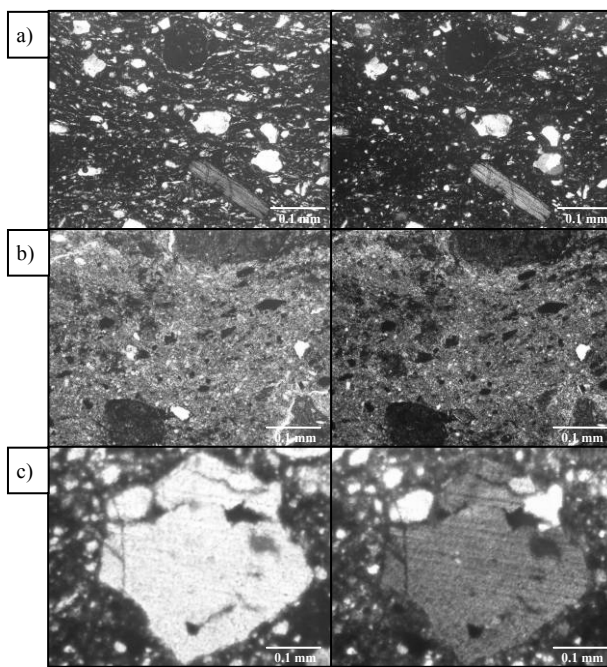


Fig. 2.: Microscopic photos of ceramic samples number: a) NIEM/05/199/a, b) NIEM/05/161/a, c) NIEM/05/150/a taken with 10x enlargement in transmitted and reflected light. Photos: a) petite admixture of a “thin” ceramics with 0.18 mm organic piece, b) ceramic mass of a “hard” ceramics with ferruginous grains of old ceramics, c) 0.4 mm angular grain of plagioclase in a “thin” ceramic sample.

Another part of the presentation will be associated with the general condition of the ceramic petrography in Poland. Whereas expanding in some European academic centers (especially in British geoarchaeology), condition of ceramic petrography in Poland is still in a prior state. Several researchers have recently started to introduce this discipline into archaeology (Łaciak, 2007) unfortunately basing mostly on the ordered research. On the other hand geological scientists are usually more concerned with stone remains than ceramics. As a result of these reflections, another aim of the presentation is emphasis of the importance of conducting this kind of research in the geoarchaeological environment.

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## Petrographic study of jacupirangite from Kerimasi volcano, Tanzania

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Carbonatites and associated silicate rocks are one of the most exciting and complex branch to examine petrographically and geochemically. The study of these igneous rocks has an outstanding significance as they are of important mineral sources of rare earth elements (REE+Y) and some high field strength elements (HFSE) such as Zr, Nb, Ti, Ta.

The Kerimasi volcano is located in the Gregory Rift Valley along the East African Rift System, in the northern part of Tanzania, near to the Oldoinyo Lengai volcano. Jacupirangite, like other plutonic rocks in Kerimasi, occur as blocks in the volcanic agglomerates (Dawson, 2008).

For detailed petrographic study we carried out optical microscopy, scanning electron microscopy and HR-Raman microanalyses on the samples. The jacupirangite is a plutonic rock that shows cumulate texture and consists of dominantly clinopyroxene (diopside) with abundant amount of magnetite and calcite. Accessory minerals are phlogopite, apatite, olivine and pyrrhotite. Calcite forms euhedral crystals or appears interstitially. In some cases dolomite can be observed as intergrowth of calcite. Based on the optical microscopic and SEM observations, both the diopside and magnetite are rich in crystal and irregular shaped, randomly distributed melt inclusions (10-50  $\mu\text{m}$ ). SEM and HR-Raman spectroscopic measurements proved that diopside contains magnetite, apatite, calcite, phlogopite, badelleyite and Na-Ca-K carbonates, whereas magnetite contains diopside, apatite, phlogopite, calcite, dolomite, badelleyite, perovskite and Na-Ca-K carbonates as crystal inclusions. Apatite in diopside and magnetite is strongly zoned displayed on CL images (Fig 1).

Selected double-polished single grains of diopside were heated up to 1000  $^{\circ}\text{C}$  in a heating stage to determine the homogenization temperatures of melt inclusions that occurred between 800-950  $^{\circ}\text{C}$  with the homogenization of the fluid bubble into the melt phase. Furnace technique was applied on magnetite grains to produce homogeneous melt in the inclusions. The quenched inclusions were exposed and analysed by SEM. Magnetite hosted melt inclusions are Na-Ca-K carbonate melts, sometimes containing accidentally trapped crystal phases (apatite, phlogopite, and perovskite) (Fig. 2).

The absence of silicate melt inclusions in magnetite suggests that during the formation of magnetite a carbonate melt phase was present. Based on previous studies by Guzmics *et al.* (2011) we assumed that these carbonate melts in magnetites could represent the parental melt of Kerimasi calciocarbonatite.

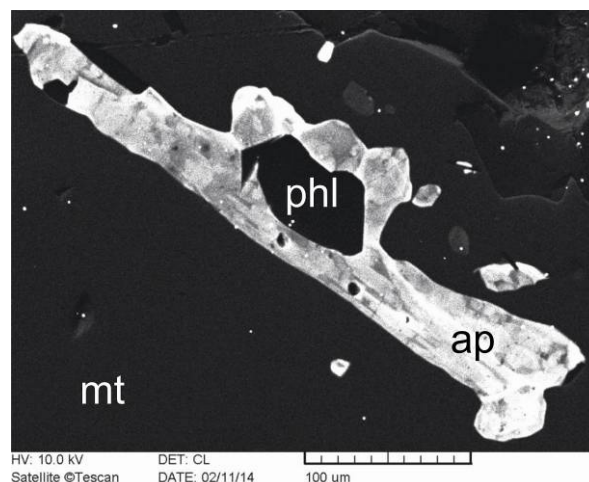


Figure 1. Cathodoluminescence image of magnetite hosted zoned apatite inclusion with phlogopite crystals in the middle. (mt – magnetite, ap – apatite, phl – phlogopite)

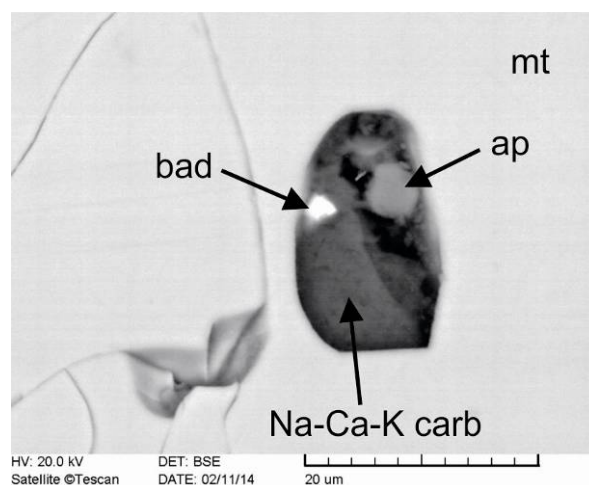


Figure 2. Scanning electron microscope image of magnetite hosted melt inclusion. (mt – magnetite, ap – apatite, bad – badelleyite, carb – carbonate)

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## Fluid inclusion study of the Reppia VMS deposit in the northern Apennine ophiolites, Italy

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The Reppia Fe-Cu-Zn sulphide deposit is one of the numerous volcanogenic massive sulphide (VMS) deposits associated with the northern Apennine ophiolites in the eastern Liguria and Emilia Romagna regions (Italy). The deposit is located close to the village of Reppia, about 50 km far from Genova. The geology of this area is connected to the evolution of the Ligurian Ocean which formed in the western limb of the Neotethys and its present-day tectonic setting is the result of the early Cretaceous-late Eocene Alpine Orogeny. The Ligurian Ocean was a slow spreading system in which from the Triassic until the middle Jurassic the intrusion of gabbroitic bodies into Proterozoic and Permian formations was continuous. In the late Jurassic MORB-type pillow basalt was formed at the bottom of the ocean (Garuti *et al.*, 2009). The stratigraphic successions of the Ligurian ophiolites differ from the classical reconstruction of oceanic crust deduced from other ophiolites of the world, because of the lack of a sheeted dyke complex and the scarcity of layered gabbro cumulates (Garuti *et al.*, 2009). Most of the known sulphide deposits in the North-Apennines are Cyprus-type Fe-Cu-Zn volcanogenic massive sulphide deposits connected to those mafic and ultramafic rocks, which represent the former oceanic crust. These deposits bear valuable information regarding the VMS ore-formation at the bottom of the sea because almost no effect of later metamorphic events can be traced (Garuti *et al.*, 2009). The aim of this study was to carry out the first detailed analysis of fluid inclusions in the sulphide ore to provide more valuable information about the origin and evolution of hydrothermal activity in the Ligurian ophiolites. For this purpose, the VMS deposit of Reppia was selected, since it contains sulphide mineralization in three different settings, within one single stratigraphic section comprising the serpentinite-basalt-sediment transition. They are: i) stratiform deposit in the ultramafic breccia at the top of the serpentinite unit (type 1), ii) stratiform deposit at the top of the pillow basalts (type 2), and iii) stockwork-vein ore mineralization (type 3) crosscutting the pillow basalt, below type-2 stratiform mineralization (Zaccarini & Garuti, 2008).

By petrography pyrite, chalcopyrite, pyrrhotite, sphalerite and detrital chromite as ore minerals and quartz, chlorite and calcite as gangue minerals were identified in the type-1 mineralization. In type-2, pyrite, pyrrhotite and minor chalcopyrite were observed as ore minerals, along with quartz, chlorite and clay minerals as gangue. In the type-3 deposit, we have identified chalcopyrite, pyrite, sphalerite, hematite and ilmenite as ore minerals, and quartz and chlorite as gangue.

Three generations of quartz were distinguished in the stockwork veins, possibly corresponding to a sequence of crystallization events. The first (earliest) generation consists of euhedral-subhedral, prismatic crystals, commonly characterized by growth zoning with a spongy core. The size of the first generation varies between 0.5 and 2 cm. The grains in the second generation are subhedral, rounded, the crystals are clear and slightly smaller (around 0.3 cm) with the absence of zoning in most of the cases. In the second generation, the grains are rounded and have a size below

20 µm. Every generation contains primary fluid inclusions, which are round-shaped and exhibit a constant phase ratio (5-10% vapour phase and 85-90% liquid phase). The primary inclusions may be connected to the growth zones of the quartz or may occur independently in the limpid crystals. The occurrence of secondary inclusions is very common. Their shape, size and phase ratio are variable. Fluid inclusion micro-thermometry measurements were done on both quartz generations and chlorite thermometry calculations based on the EPMA analyses of the chlorite were done on chlorite crystals which are syngenetic with the first quartz generation, based on petrographical evidences. Since the measured homogenization temperature values give the minimum formation temperature of the quartz, the chlorite thermometry calculations were also taken into consideration to obtain the real formation temperature (Zang & Fyfe, 1995). The formation pressure can be determined with the combination of the two methods, if the chlorite and the quartz are syngenetic. The average minimum formation temperatures were  $150 \pm 15^\circ\text{C}$  in the case of the first generation and  $145 \pm 13^\circ\text{C}$  in the case of the second generation. The observation of the final melting temperatures was often hindered by the metastability of the inclusion fluid upon cooling. Where metastability did not occur, an average salinity of 3 NaCl equiv. wt% was calculated. In the case of the chlorite cogenetic with the first quartz generation, the thermometry calculations (Zang & Fyfe, 1995) gave an average of  $198^\circ\text{C}$  as the formation temperature. The combination of these data results in a formation pressure of about 0.9 kbar, if the effects of the observed (with Raman spectroscopy) methane gas phase is also taken into consideration. This could be caused partly by the water depth, or by the thickness of the overlying rock series. To decide this, more research is needed.

Comparison of these results with the formation temperature values of several different VMS deposits ( $250\text{--}400^\circ\text{C}$ , Pirajno, 2009; Inverno *et al.*, 2008; Zengqian *et al.*, 2008) shows that the research area formed at lower temperatures. This can be explained either by the difference in the tectonic setting or by the possibly distal formation of the studied veins, in relation to the centre of the hydrothermal fluid flow.

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## Delineation of faults by 2D and 3D common depth point methods in hydrocarbon fields of Kazakhstan

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One of the major objectives of non-quantitative interpretation of seismic data is the delineation of tectonic deformations (faults). The importance of information on the presence and location of faults for the development of the fields is difficult to overestimate - they can appear as structural barriers and have a dominant impact both on the flows of recoverable oil and injected water. They also have effect on the distribution of pressure in the deposit (Ampilov, 2004). According to the data of two-dimensional seismic profiling, the faults can be reliably delineated in some points, but tracking them is extremely difficult and controversial. Delineation of faults using 3D seismic data is an important and feasible objective. However, not all faults are mappable, and the degree of reliability is always variable (Voskresenskiy, 2001).

The solution to these problems was considered by the example of the Dunga field, located in Kazakhstan, near the Caspian Sea, and confined to the western pericline of Beke-Bashkuduk swell related to Mangyshlak-Ustyurt dislocation pattern. According to the results of exploration on the Dunga structure there were found two oil fields in the Aptian sediments (A, B), one gas (IO-I A) and one oil and gas (IO-I B) deposit in the Callovian deposits of the Upper Jurassic (Fig. 1.) (Golonka, 2007).

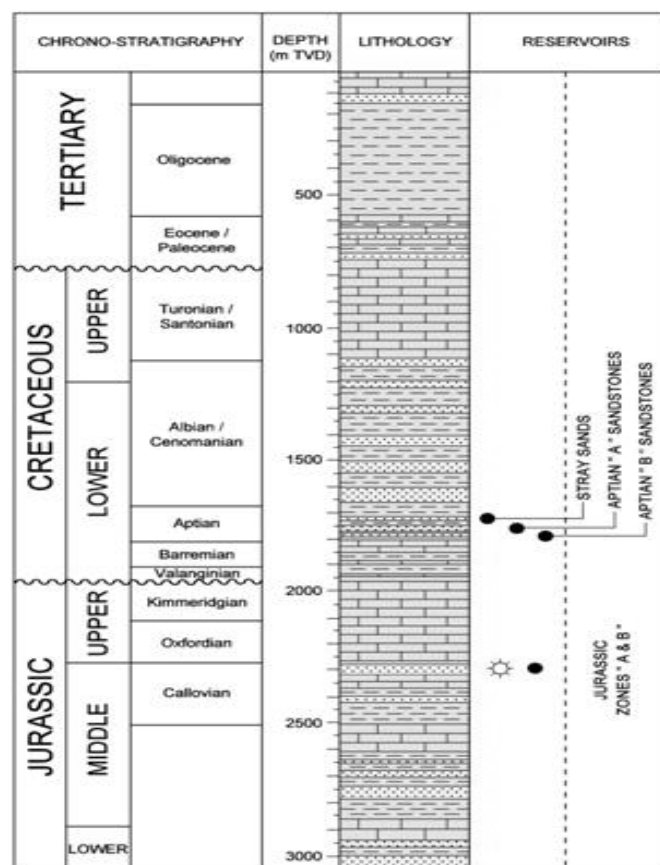


Fig. 1.: Stratigraphic section of the field Dunga.

In 1991-1992, the CDP exploratory seismic operations carried out in the area of Western Beke-Bashkuduk. For the Dunga field the top of Aptian productive reservoir structure map was developed. A set of low-amplitude transverse faults is delineated on the map, whose presence was justified previously by well test data at the stage of exploration. The occurrence of these faults according to seismic data was mostly confirmed, although small amplitudes define some convention of them. In 1997, the re-interpretation of 2D seismic lines located within the Zholaskan-Dunga-Espelisay area was carried out. As a result, the top Aptian reservoirs A and B structural maps were presented, which are in good coincidence with each other, but have more complex structure compared with the data of CDP conducted in 1991-92. The fundamental difference is in the greater number of faults. The amplitude of these faults does not exceed 10 m, and for most of them is in the order of 5 m. In 2006, another re-interpretation of previous 2D seismic data obtained directly within the Dunga field area was carried out. As a result, the general structural pattern of the field was confirmed, the Dunga uplift, which has a block structure, was revealed, the location of previously known faults (F1, F2, F3) was updated, the presence of faults (F4) in the central part of the uplift was confirmed. The occurrence of fault (F4) is supported by the test data of wells 23, 16 and logging data of well 32. Seismic faults have north-east and north-west bearing and displacement amplitude of 10 m to 15 m.

Geological model of the field required further elaboration and for this purpose, 3D seismic investigations carried out at the end of 2006, beginning of 2007. A high-quality full-offset three-dimensional seismic record was developed almost over the area of mine allotment of the Dunga field based on the results of processing of three-dimensional seismic data, which confirms the location and the overall shape of the Dunga structure and significantly details the reservoir of Aptian horizon. Interpretation of faults was conducted using variable-based and coherent data. Faults with significant dislocations were found in areas of low folding of recording on the three-dimensional seismic survey. Most likely these faults would not have been discovered without the high spatial resolution of the three-dimensional seismic survey. Previous studies have suggested that tectonic deformation in the north-south direction eastwards of the main structural closure, will appear as a sealing fault in the east of the field. It is important to note that no evidences of the occurrence of such a fault were found, either on the variable-based data, or on the seismic data.

Thus, the developed faults model can explain the distribution of hydrocarbons in the Aptian interval on the Dunga field. In particular, it is assumed that there is a tectonically screened trap in the east from the border of the mine allotment.

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## Geochemical features and isotopic age of charnockite-type rocks of Upper Pobuzhya of the Ukrainian Shield (Lityn dome structure)

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Rare earth elements (REE) are considered to be one of the best indicator components, distribution character reflects to the processes of rock formation. Based on the analysis of REE in rocks of Litynskyi and Malynivskyi quarries using ICP MS methods, using also the already published data of Lesnaya (1988), the following basic types of REE distribution were found in the studied rocks: 1) low (<50 ppm) content of REE with distinct positive Eu-anomalies, 2) moderate (100-150 ppm) REE content with positive or mild negative Eu-anomalies. 3) increased content of REE (up to 230 ppm) with small positive Eu-anomalies or without them. The first type is typical for two-pyroxene oldest Paleoarchean enderbites of the Gayvoronskyi Complex (3.6 Ga) and hypersthen enderbites of the Litynskyi Complex, which confirms the theory of formation the latter by transformation of rocks of the Gayvoronskyi Complex. The second distribution type of REE spectra is observed in vinnicites (biotite-garnet feldspar-plagioclase rocks with hypersthen). The third type of REE distribution is typical for enderbites with increased content of potassium (charno-enderbites).

The degree of REE differentiation, expressed in ratio  $(La/Yb)_N$  changes for hypersthen-containing enderbites within 5.4-79.2, at  $Yb_N = 10.7-0.87$ , at  $\sum REE = 47.5-125$  ppm. For the studied rocks weak and well manifested positive europium anomaly  $Eu/Eu^* = 1.6-4.5$  is typical.

REE in vinnicites are poorly differentiated.  $(La/Yb)_N = 2.4-4$  at  $Yb_N = 11.8-18.7$ ,  $\sum REE = 125.2-144$ . Mild positive and negative Eu-anomalies are also allocated  $Eu/Eu^* = 0.84-1.2$ .

For geochronological studies monazite was used. According to U-Pb data the isotopic age of monazite from vinnicites by isotopic ratio  $^{207}Pb/^{206}Pb$  ranges from 2013 to 1990 million years. Vinnicites are intermediate rocks between garnet-biotite (Berdychiv) granites and enderbites, where monazite age is of 2036 million years. So, perhaps, this variation of the obtained data for monazite from vinnicites is related to a small admixture of monazite from the enderbites.

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## Tracing maturity differences in catagenesis stage disperse organic matter using Raman spectroscopy

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The examination and reconstruction of thermal history in sedimentary basins is a widely used and essential discipline of geology. Numerical parameters for the reconstruction of basin evolution can be acquired by several methods (e.g. vitrinite-reflectance analysis, fluid inclusions microthermometry, etc.). Based on numerous researches and articles, the application of Raman spectroscopy might be a possible and admissible way to determine the development of the thermal history through the measurement of organic matter (OM) if it is in the metagenesis stage. Based on the previous studies, however, the measurement of diagenesis or catagenesis stage OM is more complicated because of the sensitivity of OM.

The sensitivity of OM comes from the process of biochemical and geochemical gelification that causes structural changes in the OM. With the formation of hydrocarbon the chemical composition changes constantly.

The applicability of Raman spectroscopy in maturity characterization is based on the changes of the structure of OM during the thermal maturation, which is in connection with the appearance, disappearance and change of different Raman active vibration modes during the processes. The principle of the maturity estimation is the following: the OM starts to be ordered with increasing maturity thus the area of disordered peaks on Raman spectra (Fig. 1.) decreases until the graphitic stage where only one peak at  $1578\text{ cm}^{-1}$  is detectable. The Raman spectra of organic matter, except graphite, can contain first order - G band ( $1580 - 1600\text{ cm}^{-1}$ ); D bands (which vary between  $1100$  and  $1500\text{ cm}^{-1}$ ) and second order bands ( $2450$ ,  $2700$ ,  $2900$  and  $3100\text{ cm}^{-1}$ ). The peak position, area and full width at half maximum (FWHM) of the maturity the D1 band, that is the most easily detectable D and G peaks change with maturity. With increasing on Raman spectra,

shifts towards lower wavenumber, the G band approaches to the graphitic position and the area and FWHM ratio (D1/G) decreases.

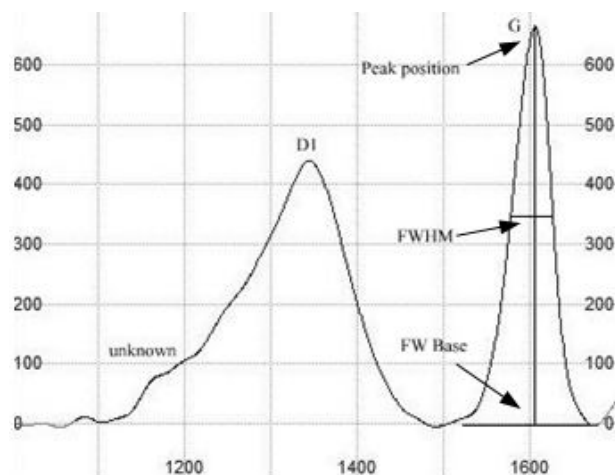


Fig 1.: Raman spectrum of disperse OM between  $1000$  and  $1800\text{ cm}^{-1}$

The present study inspects the possibility of application of the Raman spectroscopy for determination and identification of thermal history of OM situated in catagenesis stage. Raman analyses were performed on micrometer-sized disperse OM on 21 samples from different depths of a given core. The maturity of all of the samples is in catagenesis stage based on preliminary vitrinite - reflectance measurements. Based on visual kerogen analyses, the kerogen consists of type II and type III OM. The change of the FWHM ratio, integrated area and base width of G and D1 and their peak positions were calculated with the application of software PeakFit. The measurements were executed by Thermo DXR Raman Microscope.

## Paleoceanography of Oligocene-Early Miocene sedimentation of the southern regions of Ukraine

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Deposits of Oligocene-Early Miocene age (Maykop series) belong to one of the most prospective complexes of the Southern oil-and gas-bearing province of Ukraine. Their commercial oil-bearing is confirmed at Strilkova, Beysugska, Morska, Kazantypyska prospects of the Azov Sea. Within the Kerch Peninsula, the fields at Fontanivska, Pivnichnosyvashska, Povorotna, Prydorozhna, Vladyslavivska, Slusarivska (Denega *et al.*, 1998) and other prospects are related to these deposits. Within the Plain Crimea the Dzhankovske gas field is being developed. Discoveries of gas fields at Golitsynska, Pavdennogolitsynska, Shmidtova and other prospects of the north-western Black Sea shelf, as well as at Subotina prospect (Fore-Kerch Black Sea shelf) confirmed the substantial perspectives of the Maykop deposits within the whole region.

In this relation, the great importance of this study is the characterisation of the features of the Maykop sedimentogenesis, which will be the base for determination of the peculiarities of the sandy-siltstone layers spreading, forecast of the reservoir rocks and sealing horizons occurrence, assessment of perspectives of the separate prospects.

Oligocene-Early Miocene deposits are widely spread within the southern regions of Ukraine and are lacking in local areas in Dobrougea, Mountainous Crimea, in the domes of Central Crimean and Middle Azovian mega-elevation, western and eastern areas of the Northern Black Sea region. The completeness of the succession and its thickness vary significantly. The most complete succession with a maximum thickness over 4000 m has been penetrated within the Kerch Peninsula. The deposits of similar thickness of 1600-4000 m are observed within the offshore north-western and Fore-Kerch Black Sea shelves. A significant reduction of the succession completeness and thickness (up to 300-400 m) is observed within the Northern Black Sea region and the Plain Crimea, which is related to the reduction of thickness of separate horizons as well as to their pinching-out or more late erosion.

Maykop deposits are usually unconformably resting on the carbonate rocks of Eocene age and in turn are unconformably covered by the terrigenous Miocene rocks.

Stratigraphic division of the Maykop Series is rather problematic because of the similar lithological composition of the sequence, lack of the regional markers, poor paleontological remains and is made usually by electrometric data.

The base of the lithological structure of the Oligocene-Early Miocene sequence is made up of clayey rocks, which differ by aleuritic-psammitic or carbonate material. In upper, middle and lower horizons of the sequence the streaks of siltstones and sandstones are traced, whose role increases while approaching to the denudation areas. In this respect, in Maykop sequences of the axial zones of North-Crimea and Indolo-Kubanien depression the clayey lithotypes are predominant, while at southern slope of the Ukrainian monocline and north-eastern closure of the Mountainous Crimea the aleuritic-psammitic rocks are dominating. Between

these zones the content of aleuritic-psammitic material depends exclusively on the activity of temporary streams. The streaks of carbonate (marl, limestone) and silica (opoka, spongolite) rocks are also revealed in the sequence, more seldom the horizons of glauconite, siderite-bearing, ferrous-manganese rocks are traced, which are more typical for the northern parts of the region.

As for oil and gas prospecting the clastic sequences are the most important ones, the geological-paleoceanographic investigations were directed to the determination of peculiarities of their sedimentogenesis. As a result, a range of schemes have been constructed, which show the sedimentary environments for five aleuritic-psammitic lithological complexes.

Taking into account the global paleoceanographic situation in Oligocene (Zonenshine *et al.*, 1987), as well as the results of our investigations, we can conclude, that the sea transgression to the Black Sea – Azov region was moving in north-eastern direction from the East- and West Black Sea troughs through the straits in Kilian-Kalamitian-Crimean-Caucasian zone of elevations to the axian zones of Karkinite-North Crimean and Indolo-Kubanien depressions with a consequent advance into the Plain Crimea, Western and Eastern Black Sea region. Two basins with different dynamics and depositional environments are distinguished rather clearly: internal (Odessa, Kerch) and external Black Sea, which were separated by the Kilian- Kalamitian-Crimean-Caucasian range of submarine-surface elevations.

In the external part, it is open for the oceanic water, thus the deep-water conditions were predominant in the Black Sea sedimentary basin. The depocenters of sedimentation were spread within the East- and West Black Sea troughs and the clayey, more seldom aleuritic-clayey muds deposited there.

In the internal part, in the Odessa and Kerch Basins, the near shore-marine and alluvial-deltaic sedimentary environments prevailed. Terrigenous sedimentation dominated there (aleuritic-clayey muds, sands, aleurites). Detritic material was derived by a range of river systems (Pre-Dnister, Pre-Dniipro, Pre-Molochna, Pre-Don). The latter supplied generally insignificant volumes of clastic material, which in our opinion was caused by the peneplainized type of denudation areas. However, they had a rather essential influence of the way of clastic material distribution, forming psammitic-aleuritic node bodies of facial zones: "river bed", "river mouth bar", "fan", "along shore bar", though they are insignificant in area and thickness.

In the areas of the maximum subsidence (Mykhailivska, Nyzhniogirska, Shubynska, Bagerovska depression) the aleuritic-clay and clayey mud of the outer shelf were formed.

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## Possible use of geophysical methods in exploration for Pb-Zn deposits in Kosovo

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The principal role of geophysical prospection is to understand the physical features of rocks and minerals. Application of electric and electromagnetic methods is successfully used in prospection of Pb-Zn sulphide deposits. Different rocks exhibit different values of electrical resistivity. The sulphide ore is characterized with low resistivity that stands out from the surrounding rocks.

Base-metal deposits in Kosovo are of particular value. The lead-zinc deposits have been extracted since pre-Roman times. Actually the lead-zinc ores are extracted and processed by Trepça Mining Complex. Trepça, as well as several other companies are presently the holders of prospecting concessions. The whole area has a high prospection potential, because of the fact that in the last years a few new mineral occurrences have been discovered. The recent political stabilization in Kosovo provides good conditions for carrying out field research, including the application of modern geophysical surveys.

Overall site investigation and knowledge about regional geology plays the key role in successful prospection. The Pb-Zn deposits in Kosovo are located within the Vardar Zone (Schumacher, 1950; Hyseni *et al.*, 2010). The metallogenesis was related to Tertiary calc-alkaline volcanism activities.

Stan Terg, the largest Pb-Zn deposit in Kosovo, is of metasomatic-hydrothermal origin (Palinkaš *et al.*, 2013). The ore bodies are hosted by schists and carbonates, on a contact with volcanic rocks. Principal ore minerals are pyrite, galena, sphalerite, whereas minor minerals are pyrrhotite, arsenopyrite, marcasite, chalcopyrite, as well as many other sulphides and sulphosalts. The gangue minerals are calcite, quartz, dolomite, and rhodochrosite. The ore is mainly massive and coarse-grained.

The other known lead-zinc deposits of Kosovo, like Novo Brdo, Hajvalia, are characterized by similar features. Kizhnica and Crnac deposits are related to serpentinites. All the Pb-Zn deposits in Kosovo are mainly replacement deposits in carbonate rocks, sometimes skarn occurs. Veins and veinlets, paleokarst fillings, ore lenses, disseminated sulphides are also common.

The suitability of the application of different electrical and electromagnetic methods in the Stan Terg deposit area has been considered. Among these methods are the direct current method (DC), induced polarization (IP), time-domain electromagnetic (TEM), and audiomagnetotellurics techniques (AMT). The last two of them may allow investigating also greater depths. The Stan Terg deposit is open towards the depth, and the length of the deposit is also uncertain, therefore the study of deeper rocks plays a key role in prospection.

Modeling by the IX1D software has shown benefits of investigation by each considered method and also limitations of them. The forward modeling problem has been solved. Layered geological model and values of physical parameters have been selected. Finally, the obtained synthetic data for each method have been compared.

The chosen geological model comprises layers of carbonates, schists, volcanic, volcano-sedimentary rocks, as well as sulphide ore. Orebodies are located between carbonates and volcanics. They are lens shaped. The resistivity and polarization values have been set as in the laboratory measurements done by Korolija (1980).

Carbonates and volcanics show the highest resistivity; and also the other rocks have rather high values of this parameter. The ore is characterized by approximately the same value of resistivity as schists and volcano-sedimentary rocks (about 300 ohmm), what is greater than typical (30 ohmm). Therefore two models with different ore resistivity have been considered, with resistivity values of 300 ohmm and 30 ohmm, respectively.

The relatively high value of ore resistivity could be caused by picking up not representative samples for measurements, by high content of sphalerite in the investigated samples, by mistakes during the measurements or because of using outdated equipment.

Last but not least, the time of polarization was set. The sulphide ore stands out with long time of polarization (30 ms), whereas the other rocks are characterized with values lower than 10 ms.

The result has proved how large the influence of resistivity value of the ore is. The identification of orebodies is possible only when they strongly stand out with low resistivity. If the resistivity of ore is only about 30 ohmm, we can observe a resistivity anomaly and its contrast towards the surrounding rocks. Then the surrounding rocks have similar resistivity values that may cause difficulties in distinguishing the borders between ore and non-mineralized rock.

The high resistivity of rocks is a limitation for time-domain electromagnetic technique. Good results have been obtained by modeling for DC, IP and AMT methods. The AMT method should be used to identify physical features at greater depth, to a few kilometers, what is sufficient for mining and economic geology purposes.

In the Stan Terg area the successful geophysical survey may be conducted only if the ore is of low resistivity. Otherwise the measurements will not give satisfactory results and it will not be possible to uniquely identify the orebodies.

Properly conducted electrical and electromagnetic surveys in Kosovo may be helpful for carrying out base-metal prospection and to indicate the optimum sites for drillings. However, the key is first to perform accurate laboratory measurements, to see the physical characteristics of the studied rocks.

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## Geological and geomorphological analysis of Doren Landslide (Vorarlberg, Austria) based on high resolution UAV and TLS DTM

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Digital elevation data computed from Unmanned Aerial Vehicle (UAV) imagery and Terrestrial Laser Scanning (TLS) are characterized by very high resolution and high accuracy. In order to make use of this data quality it is getting more and more important that we find effective ways to process and evaluate these DTMs for detailed geological, geomorphological and geomorphometric analysis. This kind of analysis can reveal micro-topographic features and tectonic faults not observed in the field.

The aim of our study is to map the range of information that can be extracted from high resolution UAV and TLS DTMs and compare them with the field observation data. During the quantitative DTMs analysis we get the opportunity to derive geomorphometric parameters and the elements of the landscape can be analysed further, e.g., can be divided into topographic domains.

The measurements were carried out at the Doren Landslide (Vorarlberg, Austria). This landslide situated in the Alpine molasse foreland. Geological field observations indicate some subrecent faulting activity with typical fault direction WSW-ENE. Several formations (Kojen Formation, Würmian glacial moraine sediments, Weissach Formation) were tectonized there (Oberhauser *et al.*, 2007). The sediments are characterized by varying grain sizes providing material for the different parts of the creeping and moving parts of the landslide at various rates.

The UAV measurements were carried out simultaneously with the TLS campaign. The UAV data acquisition focused just on the landslide scarp. The original image resolution was 4 mm/pixel. Image matching was implemented in pyramid level 2 and the achieved resolution of the DTM was 0.05 metre.

The TLS dataset includes 18 scan positions and ca. 300 million points for the whole landslide area have been acquired. The calculated DTM has 0.2 meter resolution after the removal of vegetation points via a hierarchic robust interpolation method (Kraus & Pfeifer, 1998).

The two types of DTMs were analysed with OPALS (Pfeifer *et al.*, 2013).

The UAV DTM point density was more homogenous than TLS datasets where the point density depends on different scan positions.

SigmaZ value showed the reliability of the DTMs. Both model sigmaZ values (sigma value of residuals of each fitted planes) were under 0.01 m in the flat area but in the steep slope area had higher value (0.1 m). UAV data had some image matching problem where the texture did not show enough characteristic variations.

Aspect and slope parameters extracted more information about the geomorphological features, especially about toes of small internal sliding/creeping surfaces.

Visualizational interpretation of the datasets separated clearly scarp, selective denudation area (incipient incision) and different faults and rills. The TLS datasets reveal the surface under the vegetation to some extent and provided more geological information not accessible for the field work.

Both datasets provided linear features interpreted as displacements and eventually fault boundaries for the different hard surfaces. In the area of the toe such linear features are related to the creeping/plastic motion of the material of the landslide. Furthermore, on and along the scarp surface some tectonic activity indicators can be extracted, too.

Using the different derivative parameters of the DTMs we made a multi-channel (aspect-slope) raster database and applied ISODATA classification method for the study area in order to extract geomorphometric units automatically. The results were correlated with the Zámolyi & Székely (2009) interpretation study.

The conclusion is that both high resolution DTMs are able to represent interesting micro-topographic features. This study showed, what could be the advantages and reliability of each types of models. If the measurements are regularly repeated in the future, we can detect how the landslide develops and what happens to the features detected in this study. This knowledge will help to understand the movement of the landslide.

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## Geological Applications of the Electrical Borehole Imaging

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Electrical imaging log is an excellent tool in geological interpretations of well data. It can be used to identify natural fractures, faults, unconformities, bedding dip angle, dip azimuth, grain size and shape which allow analysis of sequence stratigraphy and facies reconstruction. Due to high vertical resolution this tool is particularly helpful in the thinly laminated sediments e.g. shale rocks. This method is becoming increasingly important in interpreting the subsurface structures and helps to reducing costs for oil and gas exploration.

The electrical borehole imager is a wireline tool with six independent arms which 25 electrodes per 1 pad, it gives 150 measurement points (XRMI™ Tool [http://www.halliburton.com/public/lp/contents/Data\\_Sheets/web/H/H03629.pdf](http://www.halliburton.com/public/lp/contents/Data_Sheets/web/H/H03629.pdf)). The effect of the measurement is a resistivity image of borehole wall of high vertical resolution (0.5 mm). Resistivity imaging device is measure in fact the resistivity contrast between different features on the borehole wall like beds, matrix-clasts etc.

Examples of the geological features from a single well in the Ventura basin, California, contain excellent models of sedimentary features such as groove casts, lenticular bedding, scours graded beds, and rip-up clasts (Amer et al., 2011). These examples (Fig. 2.) allow interpreting geological facies such as turbidities and channels of the continental slope.

Electrical imaging tools were developed as advancement on dipmeter devices where each arm records microresistivities of the formation in the borehole wall, it provides data used to compute formation dip. The results of computer processing are most frequently presented as a vector plot (Fig. 1. track 2.). This application is included in electrical borehole imaging tool as well. As an example the combination of electrical imaging and vector analysis of which geologists are enable to interpret e.g. eolian facies (Fig. 1.).

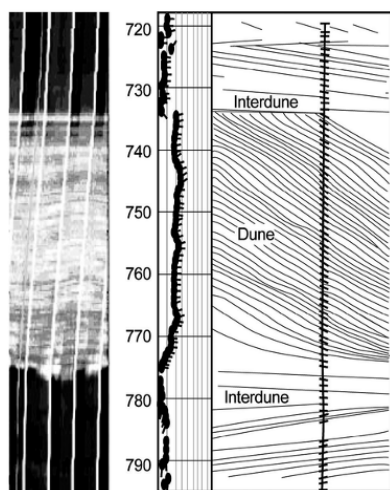


Figure 1.: Track 1: example of an electrical microimage, track 2: vector plot and a scheme of layer dip shows inner geometry of the eolian and interdune sands (source: petrowiki.org/File%3AVol5\_Page\_0404\_Image\_0001.png)

Further source of information, while considering this group of tools, is the possibility for estimates of borehole diameter. All arms of the tool are pressed to the wall of the borehole creating signal that represents the changing shape of the borehole. The change of the diameter can indicate the change of the lithology (e.g. washout over the evaporate layer), evaluate and orient borehole breakouts and man-made caverns caused by drilling process.

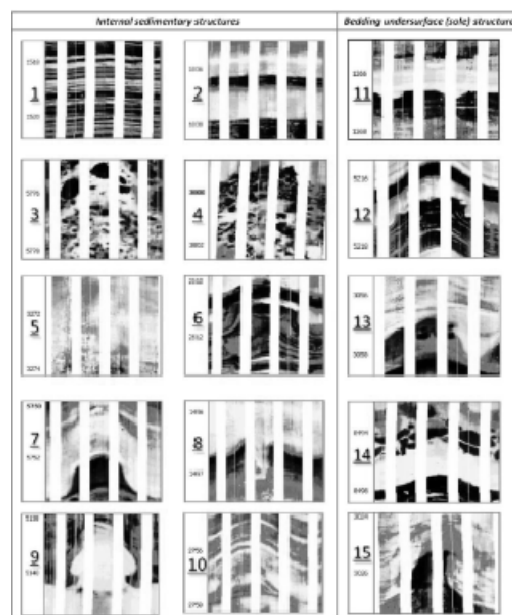


Fig.2.: Sedimentary structures observed on the high-resolution borehole image logs. (depth in feet): 1,lamination; 2,bedding; 3, inverse/reverse grading; 4, conglomerate; 5,massive bed; 6, convolute bedding (slump); 7, sediment deformation; 8, water escape structure; 9, sand injection; 10, cross-bedding; 11, groove cast; 12, load cast; 13, small-scale scour surface; 14, erosional channel base with lag; 15 ,flame structure (Amer et al., 2011)

The electrical borehole imager is a great source of geological information, no previous well logging tool could offer such various set of geological data. Borehole image data are used for the identification of lithology, depositional environment, paleocurrent direction, giving great value in interpretation model of the reservoir.

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Courtesy of Schlumberger (FMI™ [http://www.slb.com/~media/Files/evaluation/brochures/wireline\\_open\\_hole/geology/fmi-hd\\_br.pdf](http://www.slb.com/~media/Files/evaluation/brochures/wireline_open_hole/geology/fmi-hd_br.pdf))

## Development of subsea separation system for multiphase pump

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We propose to introduce the vortex type separator of gas and hydrocyclone of water separation in traditional system of separation and redesign or improve the multiphase pump (MPP) for: minimizing the dimension and mass of the gas separator; collecting the sand in separate tank, enhancing the properties of screw material of the pump by decrease of hydro-abrasive wear. The mathematical model for proposed construction of separator is elaborated.

The ideal system of separation and pumping must ensure separate pumping of multiphase medium components (fluid-gas-water-solid, usually sand) from oil well and transport the material to 10 mile distance and more. This system must have high reliability with no failures within 10 years on the sea bed up to 4000 m depth. We consider equilibrium of droplet which is located in flow gas-liquid mixture, and the analytical expression to determine its limit radius.

For the experimental studies of separator an experimental pilot plant was designed and manufactured. Pilot installation performs the following functions:

1. Provision of research separator in conditions close to real (industrial);
2. Providing of modelling for different modes of separator;
3. Ensuring measurement of the test separator;
4. Ensuring the safety of personnel during the experimental studies.

In order to optimize the design of the separator and the inclusion of its original structural elements that improve the technical performance of the gas vortex separator (inertial) type the computer models of the separator that simulated real conditions of operation were carried out.

Separation and MPP may give same advantages: longer life of MPP, higher efficiencies. Some companies (FMC, Statoil) apply systems of separation and MPP. There are many possible configurations of systems: with separation of water and its injection into the well, periodical collection of sand and removal it on the platform, etc.

Our proposal is based on the application of hydrocyclone to remove sand to special rubber reservoir, which may be changed periodically after its filling by sand (Fig. 1.). Hydrocyclone may also separate water from fluid.

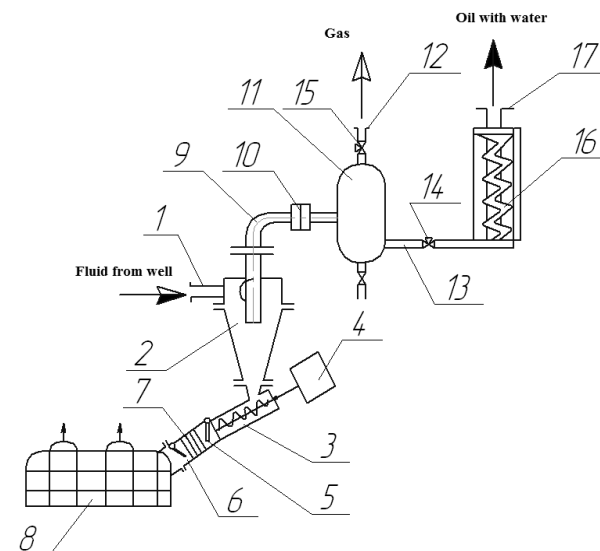


Fig. 1.: System of sand and gas separation before entering twin-screw pump  
1 - pipe for reception of the fluid from the well, 2 - hydrocyclone unit for solids separating, 3 - screw for solids moving; 4 - screw drive mechanism, 5 - the valve of screw mechanism, 6 - valve of rubber tank, 7 - mechanism to be able to transport solids to the surface, 8 - rubber reservoir, 9 - outlet of the fluid-gas mixture with solids; 10 - valve or shut-off unit, 11 - gas-liquid vortex -type separator, 12 - pipe for gas exit, 13 - pipe for displacement of purified liquid, 14, 15 - locking elements, 16 - twin-screw pump, 17 - pipe for exit of purified liquid product.

Vortex type gas separator may be used also for gas or for the sand separation. The new system of gas and sand separation with MPP is proposed. Gas after separator is directed to compressor and pumped to platform or FPSO by umbilical. Sand is collected in sand tank.

New system of separation with multiphase pump is proposed. New type of vortex gas separator is proposed for use in this system. The mass and dimensions of new separator is 15 times less, than usual one.

## Structures of deformations of the platform cover, caused by shear displacement in the basement

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In this paper, the shear displacement in the basement and its reflection in the sedimentary cover on the example of the Aral-Kyzylkum shaft located in the north of the Turan plate are presented.

The history of evolution of ideas of the geological structure and tectonic position of the shaft is very interesting. At the beginning of the 20<sup>th</sup> century, many researchers believed that the studied shaft is an inherited structure, in other words, underneath there is the Paleozoic basement outshot. In the second half of the 20<sup>th</sup> century, N. Ya. Kunin supplied the first seismic work in the Aral Sea area. Then, it was found that the shaft has the form "biconvex lens", in other words in its structure the uplift of the upper horizons of the Mesozoic and Cenozoic strata and the deflection of Triassic and older rocks can be observed. In petroleum geology these structures are often called inversion.

In 2010 the company "Lukoil Overseas" provided us with "fresh" 2D-seismic data along the southern segment of the Aral-Kizilkum shaft. Based on the detailed analysis of the seismic data, a three-dimensional model of the deep geological structure was created, consistent with the phases of the development. The interpretation of the tectonic structures was led by modern tectonophysical ideas about the laws of development of shear deformation in the sedimentary cover. Creating a geologic model included the following stages of analysis of the geological situation:

First, the allocation of structural-material complexes was done. With this step, the basement, an intermediate complex and a sedimentary cover were received. The allocated systems met consistent tectonic regimes in the region's history: a difficult, eformed Hercynian basement, Late Cimmerian (Triassic-Early Jurassic) rifting and Alpine (Late Cenozoic) deformations. This multilevel structure is a typical characteristic of the Scythian-Turan platform.

Then in the seismic massif the main reflectors were isolated and correlated: Lower Cretaceous (K1nc) and Upper Jurassic (J3). A correlating horizon was also related to the Upper Permian – Triassic (P3?-T). The last horizon is not stratigraphical, and bears in itself purely structural sense, separating a sedimentary cover and an intermediate complex from the basement. Also it should be noted that within this horizon, the most ancient Cimmerian deformations are connected with relatively young Alpine K1nc and J3 horizons.

The next correlating horizons are J3 and P3?-Tm which build a structural surface, the combination of which is considered as three-dimensional model of the southern segment of the Aral-Kyzylkum shaft (Fig. 1.). The figure shows that the surface of P3?-T revealed graben structure, located directly under the shaft, a dedicated J3 surface. This confirms that the considered regional structure really

looks like "biconvex lens", in other words the inversion of the structure occurs.

Secondly, tracing of faults was satisfied with the formation of the three-dimensional fault unit frame crust. It can be found that the faults within the roof of the Aral-Kyzylkum shaft are grouped into positive "flowering structure" characteristic manifestations namely shear deformation in the sedimentary cover associated with shifts in the underlying folded basement.

On the seismic profiles it was also noted that the board Early Cimmerian graben and uplift in the central part are stress concentrators, of which "grow flowering structures" occur. Other features are the faulting of the sedimentary cover, which is general characteristic for the manifestation of shear strain. The regional Aral-Kyzylkum shift belongs to a late stage of development of the main fault plane, dissecting the entire profile of the sedimentary cover. Other marked characteristic of the various changes is the amplitude of displacement along faults at different depth levels of the mine. The bottom of the offset is almost not observed (mainly lateral shear displacements), and the top is also the same - they are quite clearly seen. Height also varies penetration gaps in the sedimentary cover. This fact can not mark the time of faulting, it just shows their rank.



Fig.1.: Three -dimensional structural model of a segment of the Aral-Kyzylkum shaft

Morphology of discontinuous fans indicates that the tectonic uplift of the Aral-Kyzylkum shaft is positive alpine structure formed directly above Early Cimmerian graben system.

Consideration of the segment Aral-Kyzylkum shaft like structures caused the regional shear deformation, which led to changes in views on the structure of such oil and gas shafts. Earlier this shaft was seen as anticline, but now we see it is a complicated block structure.

## The features of the evolution of oysters

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The problem of the oysters' evolution and phylogenetic relationships between them were considered in several papers (Cheltsova, 1969; Pugaczewska, 1971; Stenzel, 1971). Taxonomy of oysters in Treatise (Stenzel, 1971) is the closest to the modern taxonomy (Carter et al., 2011), but it has also gone through many changes. New data had allowed revising time boundaries of large oyster's taxa existence. The recent discovery of *Crassostrea tetoriensis* in Callovian deposits in Japan (Komatsu et al., 2002) increases the range of existence of Crassostreinae subfamily from Early Cretaceous to Middle Jurassic. Thus subfamily Crassostreinae is older than subfamily Ostreinae. The study of the genome of modern oysters from genera *Lopha*, *Ostrea* and *Saccostrea* showed affinity of modern members of genera *Ostrea* and *Lopha* and their distance from the genera *Crassostrea* and *Saccostrea* (Foighil, Taylor, 2000). These data prove the validity of the isolation of Mesozoic *Lopha*-like oysters in a single family (Carter et al., 2011) and the lower time boundary shift of the modern Lophinae existence to Miocene (Malchus, 1998).

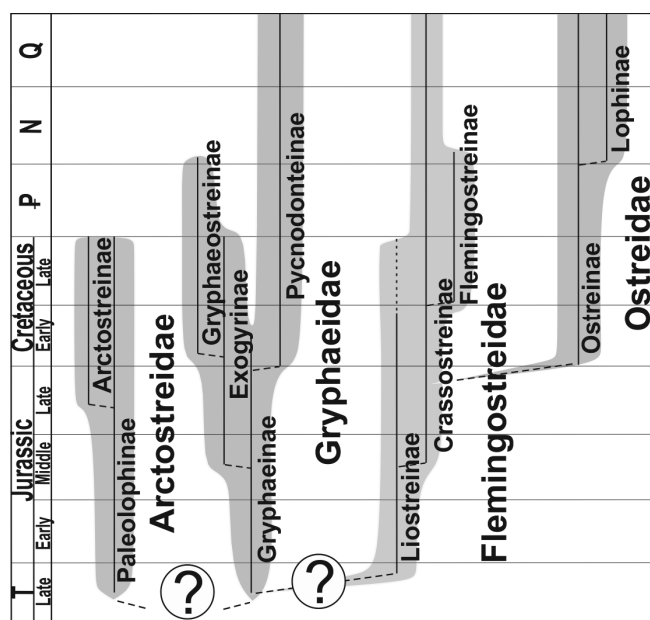


Fig.1.: The model of phylogenetic relationships of superfamily Ostreoidea.  
(based on taxonomy in (Carter et al., 2011))

The model of phylogenetic relationships of large oysters taxa (subfamily and above) based on recent data is presented in figure 1. Based on it, the main stages in the evolution of oysters can be traced. First oysters appeared in Late Triassic. In Carnian *Gryphaea* appeared in the Arctic Basin and Paleolophidae appeared in the Tethys and Paleopacific. During Rhaetian *Liostrea* had settled in the European region. The question about polyphyletic or monophyletic origin of Paleolophidae and Gryphaeidae still remains disputable. The origin of *Liostrea* from *Gryphaea* is also debatable. In Early Jurassic *Gryphaea* migrated from the Arctic Basin and started expansion in Europe. A rapid diversification of oysters began in Middle Jurassic: first Exogyrinae (ubiquitous *Nanogyra*) and

Crassostreinae (in Paleopacific) had appeared. On the Jurassic/Cretaceous boundary dramatic reducing of Gryphaeinae diversity took place, Exogyrinae diversification began and first Pycnodonteinae and Ostreinae appeared. An interesting feature is the independent appearance of chomata in different branches of oysters (Exogyrinae, Pycnodonteinae, Ostreinae). Late Cretaceous is the golden age of oysters, the highest generic diversity is observed. By the end of Cretaceous - beginning of Paleogene, Exogyrinae and Arctostreidae almost all completely extinct. Further flourishing of Crassostreinae and Ostreinae had been occurred during the Cenozoic. Modern Lophinae appeared in Miocene. Pycnodonteinae still continues to exist up to the present day, but their species diversity is not too high.

Oysters in evolutionary terms are conservative group; their morphology has not been radically changed since the moment of their appearance. The main event that led to the diversification of oysters was the transition from an attached lifestyle to living in soft substrate (Seilacher et al., 1985). This transition happened in different groups due to different mechanisms, often leading to the new taxa creation. The change of ethology and morphology had often followed by transformations of shell microstructure. These lifestyle changes have occurred over the evolution of oysters multiple times, leading to the formation of homeomorphic taxa. The "underlying synapomorphies" pattern explains the independent appearance of chomata and chalky chambers in shell microstructure in different branches of oysters (Saether, 1979; Malchus, 1998). This model suggests the existence of a parent species with the genetic code that evolves for a certain character but does not carry the phenotype itself. Thus, only the responsible genes are inherited by descendant species, but not the phenotype. Repeated independent activation of the genetic code, e. g., triggered by environmental factors, then provides the basis for multiple parallel evolution of the phenotype in subsequent lineages. This model also explains the prevalence of oysters homeomorphism.

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# The isotopic composition of carbon and oxygen in the oysters shells from the Jurassic/Cretaceous boundary strata from Maurynia River (Western Siberia)

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The complex research of *Deltoideum* sp. oyster shells from Jurassic/Cretaceous boundary strata from Maurynia River (Western Siberia) was made. The research includes a study of shell material by optical methods and a study of isotopic ( $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$ ) and geochemical (Fe, Mn, Sr) composition of carbonate material.

The microstructure of the shells did not change by recrystallization; only small areas along the cracks in the shell show luminescence in thin sections (Fig. 1C). There is no correlation between the isotopic composition of carbon and oxygen (Fig. 1D). In the samples an increased content of Fe (710 to 1990 ppm) and Mn (250 to 660 ppm) is observed, but the content of Sr (620 to 730 ppm) indicates the absence of diagenetic alteration of carbonate material. There is no correlation between the isotopic composition of carbon and oxygen and contents of Fe and Mn. Thus, the investigated samples (from oyster shells) satisfy most of the criteria of well-preserved carbonate material (Wierzbowski & Joachimski, 2007) and are characterized by  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$ , reflecting the primary variations of the isotopic composition of C and O in the Jurassic-Cretaceous palaeocean. Data obtained from oysters with existing data from belemnites were compared (Dzyuba *et al.*, 2013).

Absolute  $\delta^{13}\text{C}$  values from oyster shells are higher than the values from belemnites. At the same time general trend of  $\delta^{13}\text{C}$  changes in the cross-section obtained from oyster shells repeats the curve obtained from belemnites (Fig. 1A). Maximum  $\delta^{13}\text{C}$  values are typical for Jurassic/Cretaceous boundary interval. The same trend is observed in other regions (Dzyuba *et al.*, 2013). This indicates global perturbations in the isotopic carbon cycle during this period. Differences in absolute values are probably caused by various carbon isotope fractionation processes during the formation of the substance of oysters shells and belemnites (oysters have an external skeleton and belemnites have internal skeleton), and possibly caused by the difference of life environments of these organisms.

Vice versa absolute  $\delta^{18}\text{O}$  values measured in oyster's shells were lower than values from belemnites. Differences between the absolute  $\delta^{18}\text{O}$  values are probably due to the different mode of life of these molluscs. However, the trend of  $\delta^{18}\text{O}$  values changes for oysters is similar to that for belemnites (Fig. 1A). This indicates the global temperature regime change on the planet at that time.

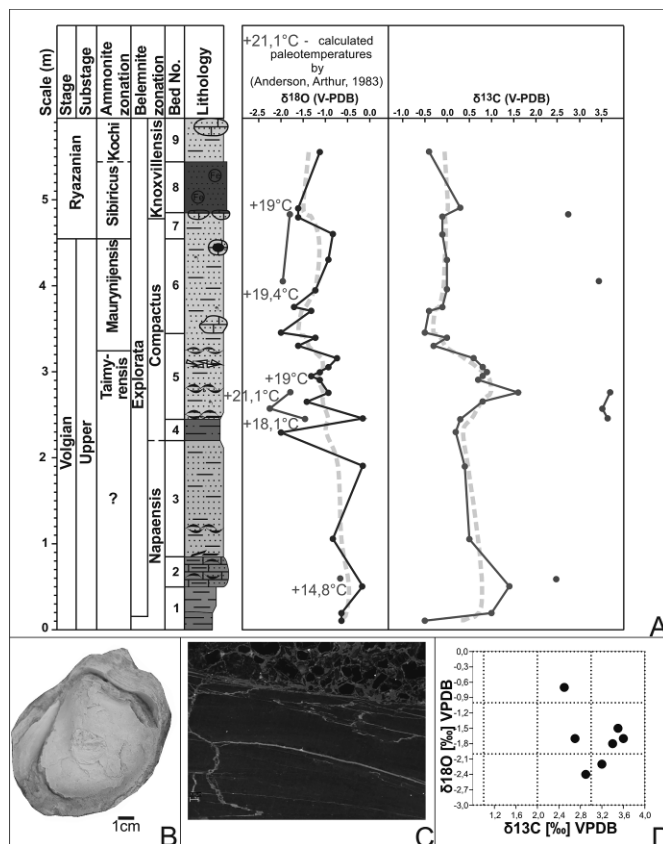


Fig. 1: A – the cross-section of Jurassic/Cretaceous boundary strata on the Maurynia river with isotopic data from oysters (this paper) and belemnites (Dzyuba *et al.*, 2013); B – the appearance of oyster *Deltoideum* sp.; C – the cathodoluminescence micrograph of oyster shell; D – the field of correlation between isotopic composition of carbon and oxygen (correlation is absent).

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## Rare earth element enrichment in the Cserkút uranium ore deposit (Mecsek Mts., S-Hungary)

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The uranium deposit of the Mecsek Mts. is located in a sandstone series and belongs to the so-called tabular subtype. The ore is found in a greenish coloured Permian sandstone sequence of fluvial origin, between the underlying grey and the overlying red sandstone series (Barabás, 1957). Northeast from this area is located the Variscan granitoid of the Mórágý Complex. This granitoid is syn-collision-type magmatic rock with a monzonitic suite (Buda & Nagy, 1995). According to an earlier study, several minerals and rock fragments of the Permian sandstone originated from this granitoid body (Barabás, 1957).

The rare earth element (REE) content of the uranium deposit of the Mecsek Mts. has been studied since the 1960s. Those studies have drawn the attention to the REE anomaly, but did not explain the possible relationship of REEs- and the uranium content and there was no agreement about the origin of the anomaly (Fazekas, 1967).

Two of the new boreholes of Wildhorse Energy Hungary Ltd. were studied in details in the frame of this research. The cores from Cserkút represent the upper level of the ore body, thus conclusions can be drawn on the REE anomaly related to this less reduced (Fazekas, 1967) part of the mineralization.

The studied boreholes penetrated the Permian sandstone, in which siltstone, fine-, medium-, coarse-grained and brecciated sandstone beds can be distinguished. The grains are mostly composed of quartz (with zircon and apatite inclusions), perthitized K-feldspar and plagioclase (suffered from sericitization), but a small amount of muscovite, biotite, rock fragments (altered granite, aplite) and accessory zircon and apatite can also be recognized. Disseminated pyrite, chalcopyrite and galena appear as epigenetic minerals as well. The matrix of the sandstone is composed mostly of sericite and microcrystalline quartz.

Chemical analyses were done to determine the uranium content, and in some cases, the REE content of the mineralized zone. In general, the more incompatible light-REEs are more enriched, than the heavy-REEs. However, in some well established zones in the upper part of the productive zone, the uranium content correlates well with the REE content. This supports the earlier assumption, that not only placer minerals of alluvial origin contain REE, but they can occur also in minerals precipitated from the uranium-bearing fluid.

In the above mentioned, well correlated zones recognized in the boreholes, the U containing minerals were found as small grains or veinlets in the matrix or in quartz and albite grains. They can be identified as U-phosphates and U-silicates (most likely autunite  $\text{Ca}[\text{UO}_2\text{xPO}_4]\text{x}10\text{H}_2\text{O}$ , coffinite  $\text{U}(\text{SiO}_4)$ , soddyite  $(\text{UO}_2)_2\text{SiO}_4\text{x}2\text{H}_2\text{O}$ ), while U-oxides were not detected.

The REE containing minerals were found disseminated or in veinlets together with the sericitized matrix or the K-feldspar grains. Florencite ( $\text{CeAl}_3(\text{PO}_4)_2(\text{OH})_6$ ), monazite ( $\text{Ce}(\text{PO}_4)$ ), xenotime ( $\text{Y}(\text{PO}_4)$ ), zircon ( $\text{ZrSiO}_4$ ) and apatite ( $\text{Ca}_5(\text{PO}_4)_3(\text{F,Cl,OH})$ ) were identified. The florencite and the monazite are enriched in light REE (La, Ce, Nd), while the xenotime is enriched in heavy REE. However, florencite may contain also some Sr and U. Furthermore the apatite and the zircon are enriched in La, Pr, and Y.

According to their textural features, the REE containing minerals may occur not only as alluvial grains, but also syngenetically with the U containing minerals.

Based on the EPMA measurements, there is a difference between the REE content of the epigenetic and detrital minerals. The results from the detrital apatite and zircon show a good correlation with the compositions measured by Buda & Nagy (1995), Buda & Pál-Molnár (2012), and Buda (2014) from the Mórágý Complex. In contrast the REE content of the epigenetic apatite is different (higher Ce, Nd, Y and lower Pr concentrations).

According to these data the source region of the detrital apatite and zircon of the Permian sandstone is most likely the Mórágý Complex. In contrast the epigenetic minerals show different REE content though their components may also have originated from the granitic body, but more research is needed to prove this.

The epigenetic U and REE bearing minerals occur together with some gangue minerals, like Sr-bearing barite and Ba-bearing celestite.

The epigenetic association of all these minerals together in the upper zone of the mineralization can occur only under rather narrow pH and redox conditions. More precisely, slightly oxidizing and neutral-to weakly alkaline environment is assumed.

On the contrary, the deeper parts of the borehole look slightly different; coffinite and U-oxides occur, accompanied by florencite and monazite of mostly alluvial origin.

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## The application of GIS tools (ILWIS) for landslides susceptibility analyse in the Polish Outer Carpathians – a case study of the Mszana Dolna area.

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The Outer Carpathians area constitutes part of Poland with the biggest landslide hazard. The Carpathians occupy only 6% of the Polish area, but 95% of all landslides in the country, which amount is about 23 000, occur here (pgi.gov.pl).

The landslide development in this area is favoured by the geological structure of basement - flysch deposits, usually with a large percentage of shale and sandstone-shale beds, as well as character of the relief – high relative altitudes and slope gradients (e.g., Poprawa & Rączkowski, 2003). The structure of the Carpathians: tectonic anisotropy of rock massifs and their fragmentation is also an important factor (Margielewski, 2001). The Outer Carpathians are characterised by the complicated tectonics with domination of forms connected with folding accompanied by longitudinal forms of discontinuous tectonics (overthrusting) and faulting of all massif.

The analysed Mszana Dolna area has complicated geological setting. From the south-east to the north-west it is crossed by the boundary of the two biggest units of the Outer Carpathians: overthrusting of the Magura Nappe onto the Silesian Nappe. In the northern part of the field deposits of the Sub-Silesian Nappe outcrop as tectonic windows of the overthrusting of the Silesian Nappe. A fragment of one of the biggest tectonic window in the Polish Outer Carpathians – Mszana Dolna tectonic window – occurs in the southern part of the field, where deposits of the Dukla Unit crop out. The lithology of this area is typical for the Outer Carpathians: layers of sandstone, shale, mudstone and marl occur in different proportions. The southern part of the area (Magura Nappe) is built of more resistant to weathering rocks, with a bigger amount of sandstone, than the northern part (Silesian and Sub-Silesian Units), which is visible in the morphology – all highest elevations are situated in the southern part of the area.

Creation of the map of landscape susceptibility as far as geological structures is concerned and connected with its morphology and hydrogeology, was the aim of the presented analysis. On the basis of the literature (Zabuski *et al.*, 1999; Długosz, 2011) the six factors which have the main influence on the landslide development in the Carpathians were selected for the analysis: 1) lithology (shale to sandstone ratio); 2) morphology (slope angle in degrees); 3) depositional dips of bedding; 4) tectonics (occurrence of overthrustings and scales); 5) hydrogeological conditions (underground water level); 6) distance from the geological formations boundaries.

The Mszana Dolna sheet of the Detailed Geological Map of Poland 1: 50 000 (Burtan, 1974), explanations (Burtan, 1978), tectonic sketch, and hydrological sketch to this map, as well as digital elevation model (DEM) of this area were used. Digitalization of maps and analysis, both vector and raster processing, were realized in ILWIS 3.4 (Integrated Land and Water Information System) software.

Maps of landslide hazard with regard to conditions occurring in the field were created for all of the six factors. Afterwards, all maps were summarized, taking the coefficients of relevance for individual factors into consideration (coefficients on the basis of: Zabuski *et al.*, 1999). The resultant map was reclassified: received results were grouped to 4 classes, where the first class constitutes slopes not susceptible to landsliding and where the fourth class is comprised of slopes with high and very high landslide hazard (after: Zabuski *et al.*, 1999).

The presented analysis showed that a large part of the studied area belongs to the class with the lowest hazard with regard to natural factors, like geology, morphology, tectonics, and hydrogeology. However, landsliding could develop even there if conditions of slopes load were worsened, as a result of following factors: construction projects, embankments, road cutting, seismic tremors, and blasting works. Areas with higher landslide hazard also occur in the studied field, and there landslides may be developed even as a result of medium or small loading of slopes.

Comparison of the analysed results and the available data about the existing landslides (Burtan, 1974; maps of the System of the Landslides Protection of the Polish Geological Institute – geoportal.pgi.gov.pl) showed general accordance between localisation of the present landslides and occurrence of the areas of the highest landslide susceptibility on the resultant map of the presented analysis. Nevertheless, it must be noticed that the resultant map shows only potentially endangered areas, whereas development of landslides usually depends on occurring or not occurring of direct, active factors, like precipitation, seismic tremors or anthropogenic activity (Zabuski *et al.*, 1999). Moreover, the comparison also showed the occurrence of some existing landslides in areas which display reduced susceptibility to landsliding according to this analysis. This can be explained by intensive anthropopression or influence of some factors which are not considered in the analysis.

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## Slag and ash as a final product of municipal waste management system

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The waste management system (WMS) is a modern way for secure disposal of waste produced in every household. Its primary aim is to protect natural environment and human health against harmful effects of waste generation and storage. Its aims are also the reduction of the amount of waste destined for storage and making maximum use of secondary materials from wastes (Sabbas *et al.*, 2003).

In the past wastes were collected and the most of them were landfilled. Increasing amount of produced wastes, limited capacity of landfill site, people concern about the environment condition and, what is also important, economic issues has forced the introduction of methods of waste managing. Waste storage is the worst solution for waste disposal. It is space consuming and do not solve the problem in general, only move it in time. Building and exploitation of landfill site is connected with the need to comply with strict regulations about environmental safety and parameters of waste possible to storage. It is difficult to predict the behaviour of the large amount of waste in a long time period and its possible influence on surrounding areas in terms of ground water and land contamination. Therefore even after closing of landfill site, it must be monitored for many years.

Nowadays wastes are source of valuable secondary materials, organic fraction and energy from combustible fraction which can be used in district heating production or electricity generation.

Building a complex waste management system is a long-term process and requires the cooperation of the government, local authorities and inhabitants of the area covered by it. In Europe, the WMS should be based on legislation in accordance with the laws of the European Community. In Poland, waste management system has been consistently formed since 1998 and some internal parts of it are still under construction.

WMS starts in every house when people are sorting their garbage which are later collected divided into several fractions. Later all of the processes connected with raw wastes processing take place. Collected fractions of wastes are resorted to separate every valuable material like paper, plastic, glass, various types of metals and organic fraction. All of these materials can be used in industry and their value has influence on lowering of the costs of waste managing. Later, residues which could not be used in different way can be landfilled or used as a fuel in incineration power plant. This facility can fulfil several tasks. Using proper technological solution it is possible to separate secondary materials from wastes (before or after incineration). Also usage of energy generated in time of incineration for district heating or electricity production is possible. Incineration plants are final elements of waste management system and their usage allow obtaining significant reduction of wastes volume (up to 70%) and mass (up to 50%).

Incineration plant produces slag and ash as final products of incineration. Raw wastes are incinerated in temperatures around 1000°C in controlled conditions in the furnace which is equipped with an exhaust gas cleaning system. Its usage reduces the amount of toxic components in exhaust gas and enables capturing of fine particles suspended in the flue gas, called fly ash.

The main product of incineration plant is heavy, incombustible fraction of raw wastes called, due to the obtained fraction, slag or bottom ash.

Composition of materials produced in waste incineration power plants varies in broad range depending on many factors specific for waste generation areas such as level of urbanization and industrialization of the area. This causes that for every incineration plant in every country obtained results are unique and cannot be comparable.

In order to characterize the final products of waste management system in Poland slag and ash samples were collected. Material was produced in municipal solid waste incineration power plant in one of the largest city in Poland. Samples were collected in 2012. The aim of this study is mineralogical and chemical characterisation of slag and ash samples with emphasis on their composition as a result of functioning waste management system in Poland.

Municipal slags are grainy materials with high silica and calcium content. They are in form of multi-element assemblages of slag material and residual fraction of wastes which were not changed during incineration processes such as glass and ceramic fragments, pieces of metals and stone fragments.

Ashes from incineration of municipal wastes are fine grained materials with similar chemical composition to slags, are also rich in silica and calcium, but more uniform in terms of fraction and general composition.

In an ideal situation, all the produced waste should be used or reprocessed. Work on the practical application of slags and ashes from the incineration of municipal waste are carried out successfully and probably in the coming years their usage will increase significantly. Slags and ashes can be used in cement and concrete production, glasses and ceramics industry and also as an adsorbent, stabilizing agent or raw material in zeolite production (Lam *et al.*, 2010, Rambaldi *et al.*, 2010, Lin *et al.*, 2003).

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# Biostratigraphy and depositional palaeoenvironment of the Cretaceous - Paleogene sediments of the Skole Unit in the Handzlówka area based on foraminiferal assemblages

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Foraminiferal assemblages of the Cretaceous - Paleogene of the Skole Unit are very rich and diverse, contain planktonic foraminifers, which are not often described from turbidite facies of the Carpathians according to the recent studies by Gasiński & Uchman (2009, 2011) and Gasiński *et al.*, (2013). Standard biozonation of Late Cretaceous- Paleogene based on planktonic foraminifera has been established (Caron, 1985; Robaszynski & Caron, 1995; Premoli-Silva & Rettori, 2002, Ogg & Hinnov, 2012). The aim of this study was micropalaeontological analysis: identification of foraminiferal assemblages, and age estimates with biozone resolution (HRS) of the samples from the Skole Unit in the Handzlówka area. Additionally, particularly important seems to be the location of the Skole Unit near the transitional zone between the Boreal and Tethyan bioprovinces (Gasiński, 1997; Marcinowski & Gasiński, 2002).

46 samples from 14 outcrops were collected from the selected section, which are mainly representing turbiditic type of sediments. As a result, 44 species of agglutinated, calcareous benthic and planktonic foraminifers were identified, dating the studied samples as Campanian – Maastrichtian, which corresponds to the Globotruncanella elevata – Globotruncanella ventricosa – Rodotruncana calcarata – Globotruncanella havanensis – Globotruncana aegyptica – Gansserina gansseri – Contusotruncana contusa – R. fructicosa standard biozones. The most important and diagnostic specimens were analysed using scanning electron microscopy (SEM) in the Laboratory of Emission Scanning Microscopy and Microanalysis field of the Institute of Geological Sciences of the Jagiellonian University (Fig 1).

Based on the field observations, lithological description have been prepared, including sedimentological features as well as tectonic structures. Based on foraminiferal assemblages the palaeoenvironmental condition of the studied deposits has been estimated to the upper - middle part of the continental slope. The tests of some specimens of foraminifers are slightly corroded which can be interpreted as probably dissolution effect causing by the by the foraminiferal lysocline.

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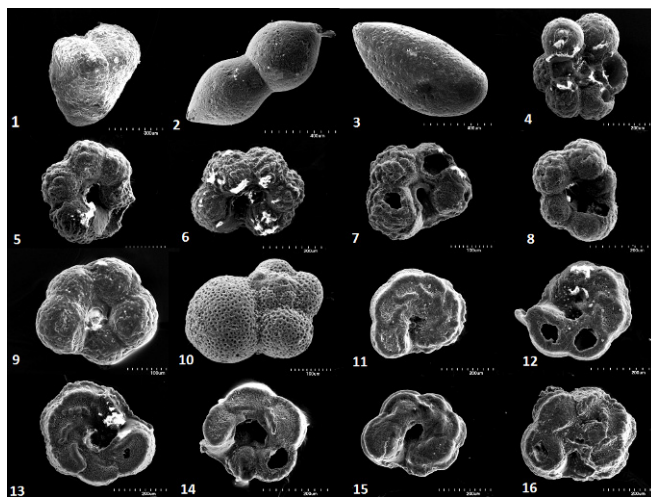


Fig.1.: 1 – *Dorothia oxycona* (Reuss), 2 – *Glandulina* sp., 3 – *Lenticulina* sp., 4 – *Archaeoglobigerina* sp., 5 – *Rugoglobigerina* sp., 6 – *Rugoglobigerina rugosa* (Plummer), 7 – *Rugoglobigerina* sp. – dissolution effect, 8 – *Rugoglobigerina* sp., 9 – *Hedbergella* sp., 10 – *Hedbergella holmdelensis* Olsson, 11 – *Globotruncana linneiana* ((d'Orbigny)), 12 – *Globotruncana arca* (Cushman) – dissolution effect, 13 – *Globotruncana arca* (Cushman), 14 – *Globotruncana linneiana* ((d'Orbigny)) – dissolution effect, 15, 16 – *Globotruncana arca* (Cushman) – dissolution effect.

# The age of basalts and gabbro-dolerite of the Mendeleev Rise (the Arctic Ocean) from data on zircon U-Pb dating

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The problem of the structure, material composition and the history of the Arctic Ocean (AO) floor is widely debated and currently central. New geological and geophysical data indicate that the floor of the Eurasian part of the Arctic Ocean overlays the crust of oceanic type, and Lomonosov Ridge and Chukotka Plateau are blocks of continental crust. The nature of Alpha-Mendeleev Ridge still remains a topic of keen discussion.

New data are discussed on U-Pb dating of zircons from basic and intermediate magmatic rocks sampled in 7 sites of Mendeleev Rise during the expedition „Arktika-2012”. First estimates of the age of those rocks appeared to be extremely contradictory and uncertain. In the basalts from the bedrocks, U-Pb age of zircons varies in a wide range: 127.5; 260; 668; 950; 1650, 1900 and 2700 million years. A similar range of U-Pb ages is noted in zircons from gabbro-dolerite fragments  $288 \pm 6$ ;  $500 \pm 5$ ; and  $761 \pm 3$  (Morozov *et al.*, 2013). Dating the same rocks with the use of  $^{40}\text{Ar}/^{39}\text{Ar}$  method (Vernikovskiy *et al.*, 2014) showed a narrower range of values ( $259 \pm 13$  –  $471.5 \pm 18.1$  million years), which allowed the authors to state PZ1 age for the Mendeleev Rise.

To solve this problem, we studied zircons from bedrock basalts that were drilled at a depth of about 2600 m and from gabbro-dolerite dragged from the slopes of Mendeleev Rise. Preparation of zircon samples separated from the above-mentioned rocks was conducted with the use of conventional methods; U-Pb analyses were carried out in TsII VSEGEI with multi-collector secondary ion high resolution mass-spectrometer SHRIMP II. Differences are noted between young and old zircons in morphology and habitus (Opt) as well as in the inner structure (cathodoluminescence – CL). The former are characterized by prismatic form of crystals, oscillatory zoning, frequent sectors in CL, missing cracks and insufficient amount of inclusions (crystals may be both rounded and for the major part unrounded). Whereas ancient zircons are elongated or elongated prismatic, have forms close to isometric, show cores in CL, roundness and considerable fissuring.

Histograms of U-Pb age of zircons and Arens-Veseril diagrams for bed-rock basalts (Fig. 1. a, b) and gabbro-dolerite fragments (Fig. 1. c, d) are demonstrated. According to the data obtained, concordant age of young zircons from bedrock basalts  $128.13 \pm 1.3$  million years corresponds to their crystallization stage and synchronous volcanism K1 abundant both in rises and islands of the Arctic Ocean. Concordant U-Pb age of late magmatic zircons from gabbro-dolerite fragments is  $151 \pm 2$  million years and corresponds to J-T times of trapp magmatism in Siberia.

The studies of isotopic composition of Nd and Sr in these rock groups (Kremenetsky *et al.*, 2014) showed the difference of basalts ( $\epsilon_{\text{Nd}}(\text{T})$  from +4.3 to +7.0;  $^{87}\text{Sr}/^{86}\text{Sr}$  from 0.70365 to 0.7049) from

gabbro-dolerite ( $\epsilon_{\text{Nd}}(\text{T})$  from – 33.1 to +2.9;  $^{87}\text{Sr}/^{86}\text{Sr}$  from 0.7050 to 0.7233), and thus confirmed that the source of bed-rock basalt matter of Mendeleev Rise had been mantle melts, which, as distinct from MORB, were formed with melting of enriched mantle in continental conditions.

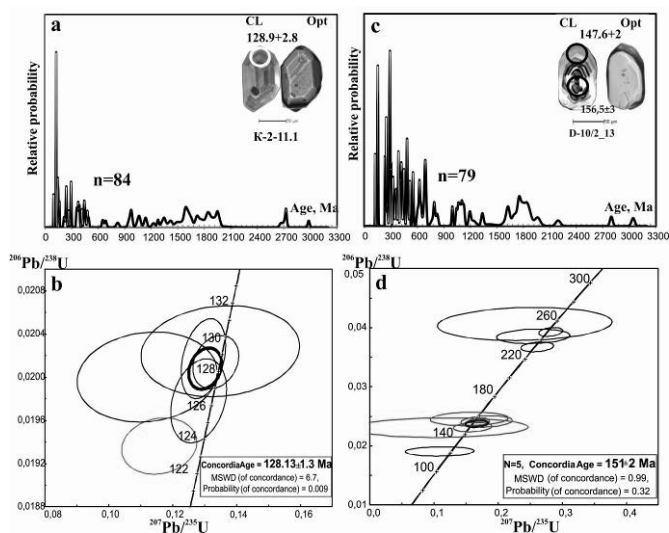


Fig. 1.: Age probability plots of U-Pb datings and diagram of Arens-Veseril with concordia of zircons from the bedrock basalts (a, b) and gabbro-dolerite (c, d).

Beside the age values characterized above, in both groups, more ancient polychronous peaks are recorded (Fig. 1. a, c) (450; 654; 1132; 1756 and 2795 million years), zircon U-Pb ages close to them (400; 700; 1100; 1650 and 2600 million years) from basalts, gabbro and alkaline volcanic rocks raised from the floor of the Central Atlantic. This may have been a consequence of contamination with young mantle melts of the ancient mantle fragments in the newly formed oceanic lithosphere or fragments of the ancient complex of the core base of the modern Atlantic Ocean.

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## Low energy coral bioconstructions from the Upper Eocene–Lower Oligocene of the Transylvanian Basin

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The Transylvanian Basin is an intra-Carpathian basin belonging to the Central Paratethys. The post-tectonic cover of marine and continental Paleogene deposits of the Transylvanian Basin comprise up to 1800 meters of sediments, including the Eocene-Oligocene shallow-marine successions. Previous studies (e.g. by I. Bucur, S. Filipescu, B. Popescu, I. Prica, E. Săsăran) revealed a relatively diversified shallow-marine carbonate facies in the Jibou area, the Salaj district, Romania in north-western part of the Transylvanian Basin. The present studies are focused on coral bioconstructions attributed to the Upper Eocene–Lower Oligocene of the Cozla Formation outcropping in abandoned quarries in Băbeni-Cuciulat and Letca. Until now Eocene–Oligocene coral reefs and smaller coral bioconstructions have not been studied in this part of the Paratethys.

The sections in Letca (40 meters) and Băbeni-Cuciulat (50 metres) consist of shallow-water deposits mostly limestones: bioclastic (mainly coralline algae) wackestones to packstones, rarely rhodolith and nummulitic packstones interbedded with some coral bioconstructions. Locally, dark, marly intercalations with plant remnants occur. Coral biostromes and low relief bioherms attain from 4 to 10 m. Scleractinian corals are common, however poorly diversified. They are dominated by thin (even 2 mm) sheet-like colonies (*Actinacis*, *Bacarella*), ramose, branching colonies (*Actinacis rollei*, *Acropora*, *Goniopora*), thin branching, quasi-colonial (phaceloid) forms (*Caulastrea*). Rarely, corals are small massive colonies (*Antiguastrea*) or have thick phaceloid growth form (*?Euphyllia*). Neither vertical nor lateral succession/zonation was recognized: thin platy colonies and branching corals co-occur closely. Coralline and peyssonneliacean red algae both encrusting and non-geniculate forms are common, while dasycladacean green algae are rare. Apart of algae, corals are encrusted by foraminifera (e.g. *Miniacina multiformis*), bryozoans and serpulids. Moreover, nummulitid, textulariid and miliolid foraminifera, as well as ostracods occur in sediment matrix. Associated macrofauna are rare and represented by bivalves (oysters, pectenids), echinoid plates and spines and small crustacean

appendages. Borings of sponges and bivalves are only locally common.

The studied bioconstructions are type of matrix-supported reefs and can be classified as spaced cluster reefs or coral carpets because corals usually do not fuse to each other, directly or by coralline algae. Low diversity of corals and other macrobiota indicates on relatively unfavorable environment for their development. Shallow and quiet-water environment is inferred based on the sedimentary sequence, dominant coral growth forms and their good preservation, the lack of rigid framework as well as fine-grained sediment matrix. Although marly intercalations are rare and low energy regime dominated, fine-grained carbonate sediment could be resuspended what resulted in increased turbidity. Branched morphotypes and quasi-colonial phaceloid corals (azooxanthellate?) are effective sediment removers or cope well with high sedimentation, and sheet/platy corals are adapted to low-light conditions. Furthermore, *Actinacis rollei* is believed to be a species tolerant to low temperature (Bosellini & Stemann, 1996 and literature herein). The studied area during the Late Eocene–Early Oligocene was located at around 43° N, thus represents one of the most northerly located coral bioconstructions in the Paratethys. Contrasting opinions exist concerning palaeogeographic control on reef distribution during discussed time interval: (1) general slight constriction in coral reef distribution; (2) significantly lower temperatures during the Priabonian (Late Eocene) favoured increased coral growth in the northern Tethys and led to the recovery of the coral fauna in the southern Tethys (see Höntzsch et al., 2013 and literature herein). The study of nummulites from the studied sequence will precise the age, providing stratigraphic framework for interpretation of local versus global/regional impact on development of the bioconstructions studied.

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## Evolution of crystal salts on level 600 in the Kłodawa salt mine

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The Kłodawa Salt Dome is located in Central Poland within the Mid-Polish Trough (MPT) area. It is the largest salt diapir which entirely pierces through the Mesozoic cover along a distance of ca. 26 km and width up to 2 km (Werner *et al.*, 1960). The salt dome consist of Zechstein salts belonging to PZ2, PZ3 and PZ4 cycles. The oldest one (PZ1) is known only as separate blocks. The inner structure of the diapir is very complicated as a result of uprise of salt members during the evolution of the salt dome and differentiated rheological, petrological and chemical properties of the various evaporate layers. The tectonic events show piercing of older salt by younger and the youngest ones, and pinching out of the layers, as well as occurrences of narrow high amplitude folds. In a general outline, two anticlines elongated in a NW-SE direction predominate in the SW and NE parts of the diapir. Anticlines are separated by the deep central syncline composed of the youngest salt layers.

During tectonic processes numerous epigenetic salts appear. They form veins and accumulations of variegated size. Their mineral composition includes large halite crystals, blue-coloured halite as well as polyhalite, carnallite and sylvite (Stańczyk, 1970, Stańczyk-Stasik, 1976, Toboła & Natkaniec-Nowak, 2008). Crystal salts are

characterized by large crystals which dimension exceeding few centimetres. They are formed as the results of intense recrystallization of halite during the uprise of rock salt. Fluid inclusion studies carried on crystals from level 600 of the Kłodawa Salt Mine showed that the formation of these salts has been possible with the participation of relatively hot fluids. Their chemical composition apart from NaCl included also large amounts of KCl and MgCl<sub>2</sub>. Such composition is proved by the presence of sylvine and carnallite daughter minerals in fluid inclusions. Crystal salts on level 600 occur together with blue salts and polyhalites. Very unusual are also fragments of birefringent halite crystals.

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## Features of Lower Triassic reservoir rocks of Vilyuy syncline (Eastern Siberia)

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Lower Triassic reservoir rocks of the Vilyuy syncline are represented by terrigenous and unconventional volcanogenic-sedimentary deposits (Dmitrievsky, 1982). They were accumulated in alluvial and deltaic (subaerial) environments. Postsedimentary transformations of metastable rock-forming components of sandy and silty intermediate-mafic tuffs and tuffites, have significant influence on the formation of reservoir properties of these rocks (Karnyushina & Zhukova, 2013).

The author studied the relationship between open porosity of the Lower Triassic reservoirs and their mineral composition on core samples from well 19 of Srednevelyuyskoe gas-condensate field, from well 4 of Severo-Lindenskaya and from well 280 of Horogochumskaya areas. Investigation of the reservoir rocks was carried out in petrographic thin sections under polarizing microscope. Open porosity of samples was determined by gas porosimeter "Ekspresspor 2000" (Ivanov *et al.*, 2008).

Terrigenous gas-bearing horizons are distinguished in Taganzhinskaya Formation deposits of the Srednevelyuyskoe field. The Taganzhinskaya Formation is represented by alternating fine- and medium-grained quartz-greywacke carbonated sandstones with subordinate interlayers of siltstone, mudstone and grussy-gravelly rocks in the upper part of the formation. There are impurities of volcanic material. Thickness of the Taganzhinskaya Formation is about 400 m. The Monomskaya Formation lies over the Taganzhinskaya Formation and composes of carbonated and zeolitized sandy tuff, crystal-vitric fine- and medium-grained tuffite, shaled out silty tuffite, subordinate role belongs to tuffaceous siltstone and sandstone (Dmitrievsky *et al.*, 2002).

Secondary mineralization causes reduction of primary pore space, formation of secondary reservoirs and often becomes a reason of reservoir to non-reservoir inversion (Dmitrievsky *et al.*, 2002; Karnyushina, 1988; Karnyushina & Zhukova, 2013). This can be demonstrated by several examples. Partial reduction of the pore space due to zeolitization is observed in tuffs (Fig. 1).

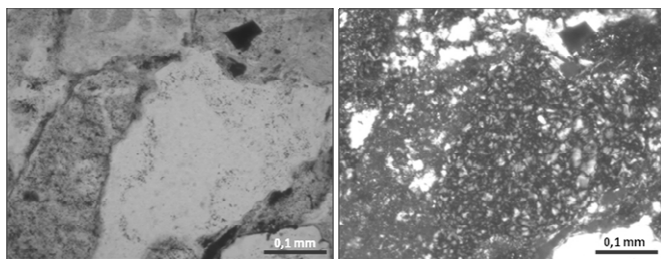


Fig. 1.: Zeolitized tuffs. Sample 69: photo micrograph of the petrographic thin section (from left to right: parallel and crossed nicols). Well Srednevelyuyskaya-19, depth 2435 m, open porosity factor 20 %.

Authigenic carbonatization leads to corrosion, partial replacement of clastic grains and complete filling pores by calcite (Fig. 2). Argillization of the tuff can provoke secondary fractured reservoir appearance (Fig. 3) or secondary seal formation.

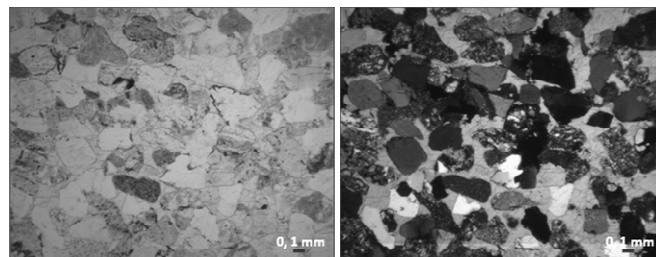


Fig. 2.: Fine-grained sandstones with secondary carbonate pore-filling cement. Sample 70: photo micrograph of the petrographic thin section (from left to right: parallel and crossed nicols). Well Srednevelyuyskaya-19, depth 2440 m, open porosity factor 11 %.

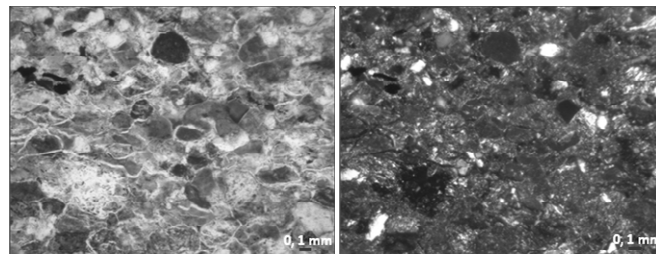


Fig. 3.: Shaled out and fractured tuffs. Sample 38: photo micrograph of the petrographic thin section (from left to right: parallel and crossed nicols). Well Severo-Lindenskaya-4, depth 1990 m.

Identified features of terrigenous and volcanic-terrigenous reservoir rock transformations indicate that the assessment of their secondary alteration is required as part of oil and gas forecast for Lower Triassic rocks of the Vilyuy syncline.

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## Archaeometric study of rock types from the Early Iron age mound grave in Regöly

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Regöly is located in the northern part of Tolna County in Hungary, at the confluence of Koppány and Kapos Rivers. The mound on the Strupka-Magyar land was discovered in the summer of 2011 and according to the archaeological finds it was built in the Early-Iron Age. Rock fragments together with artefacts were mixed with soil and deposited in the middle of the structure (Szabó & Fekete, 2011).

The goal of the research is to study the rock fragments, which are present at the site: list them into types and characterize them from the petrological point of view in order to outline the most probable provenance of the raw materials. Macroscopic description, polarizing microscopy, scanning electron microscopy (SEM-EDX) and X-ray powder diffraction (XRD) analysis were used to achieve this goal.

During field work 4074 stone artefacts were examined. According to macroscopic observations 8 main lithotypes were defined and based on the different attributes (colour, mineral composition, fabric) 27 subgroups were determined.

Based on macroscopic observations 140 representative specimens were selected for thin section analysis. Detailed petrographic analysis modified the previously established groups: 7 main and 17 subtypes were determined. The main rock types in decreasing frequency are the following: carbonate rocks, granite, sandstone, rhyolite, quartzite, basalts and basaltic pyroclastics.

Based on literary data the probable provenances of the rock types, which are present at the site are the Velence Mountains for granites, Tihany peninsula for the siliceous subgroup of carbonate rocks, Polgárdi-Kőszérhegy for rhyolites, Zamárdi for the one subgroup of the sandstones, the Balaton Highland for basalts, basaltic pyroclastics and the other subgroup of the sandstones and the Velence Mountains and/or Tihany Peninsula for quartzites. The presumption for the first four provenances has already been proven, after rock samples have been collected and examined from those territories.

Our results show that the possible provenances of most of the rock types are to the N-NW of Regöly, within 100 km (Fig.1).

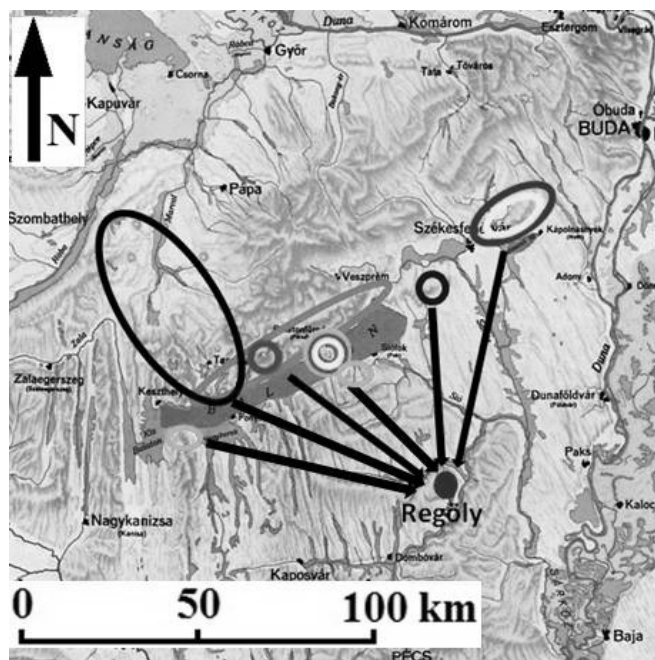


Fig.1.: The possible provenances of the rock fragments from Regöly mound; carbonate rocks: pale blue; granite: red; sandstone: green; rhyolite: dark blue; quartzite: yellow; basalt: black; pyroclastics: pink

Szabó, G., Fekete, M. (2011): *Wosinszky Mór Múzeum évkönyve* 33: 15-106. (In Hungarian)



## Conduit processes and conditions before Vulcanian eruptions indicated by blocks and breadcrust bombs: case study from Ciomadul volcano (SE Carpathians)

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In this study, the origin and importance of dacites with cracked surfaces from the Ciomadul volcano are presented. These rock types were described for the first time by Szakács & Jánosi (1989). On the basis of their macroscopic description, they suggested that these rocks can be referred to as volcanic bombs and blocks probably representing pyroclasts of an explosive eruption. The samples of my study were collected in the valleys of the Ciomadul volcano (Disznó Stream, Veres Stream) and some of them are highly similar to the samples presented by Szakács & Jánosi (1989), but additional types were also found.

According to the macroscopic analyses, two types of surface crack patterns were distinguished: Type 1: dendriform crack patterns, associated with broken crystals, could have been formed due to impact-related stress. Type 2: polygonal crack patterns which could have been the results of thermal contraction. Interior expansion of some bombs is indicated by wider, deep cracks.

According to the internal texture, the samples were classified into different groups. Breadcrust bombs are characterized by gray/white vesicular cores and black glassy rinds, the cores and rinds are sharply separated. The rind thickness varies from 0.5 cm to 6 cm. The foliated breadcrust bombs have poorly defined rinds and are characterized by the variation of vesicular white bands and black glassy non-vesicular bands. Continuous transition was observed from foliated bombs to core-rind breadcrust bombs. Patchy-banded bombs show gray vesicular matrix and white vesicular bands/patches without black glassy bands/rinds. Dense glassy dacite blocks without surface cracks and gray homogeneous blocks with

surface cracks were also found. These blocks probably have the same origin as the bombs and are related to the same explosion. Detailed study of the microlites show homogenous microlite texture and density in the different bands or in the cores and rinds. Except in the case of the patch-foliated bombs in which the white and gray patches show differences in the microlite density and vesicularity. Additionally, at the boundary of the patches flow banding and sheared crystals were also found in these samples. These features of the patchy-foliated bombs may be related to mixing of different magma batches in the conduit. This event (i.e., arrival of fresh magma and mixing with degassed magma in the conduit) might be the trigger of the Vulcanian explosion that produced the bombs. The differences of the relative proportion of the non-vesicular black-glassy and vesicular-gray or -white rinds/bands can be interpreted as the conduit depth from which the bombs originate, using the findings of Wright *et al.* (2007). According to their results, higher proportion of non-vesicular, black glassy part in the bomb suggest that it represents shallow degassed magma from the conduit, while the bombs without black-glassy portion may expelled from much deeper conduit level. Thus, the different bomb types at the Ciomadul suggest that its conduit was filled with variously degassed magma column before the Vulcanian explosion.

Szakács, A., Jánosi Cs. (1989): D S Ist Geol Geofiz, 74/1: 181-189.  
Wright, H. M. N., Cashman, K. V., Rosi, M., Cioni, R. (2007): Bull Volc, 69/ 3: 281-300.

## Ichnology of Ordovician Bukówka Formation based on Międzygórz and Mójcza section (Holy Cross Mountains, central Poland)

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The Bukówka Formation cropping out in the Kielce Block of the Holy Cross Mountains at Międzygórz and Mójcza was analysed. This area belongs to the larger structure called the Małopolska Block, which was situated on the Baltica margin during the Ordovician (e.g., Cocks, 2002). The Bukówka Formation consists mostly of fine-grained quartz-sandstone beds with local siltstone intercalations deposited during the Middle Ordovician (Trela, 2006). Most of the sandstone beds display nearly completely bioturbation (ichnofabric index 4-5 sensu Drosner & Bottjer, 1986). Primary sedimentary structures are rare. They are and represented by low-angle cross-lamination, wave ripple cross-lamination and horizontal lamination. Sedimentary features suggest a general low sedimentation rate and high degree of sediment reworking. Trace fossils are poorly preserved and low diverse, mainly due to high bioturbation. Determination of most of the trace fossils is difficult or impossible. The trace fossils contain horizontal pascichnia, including *Planolites montanus*, *P. beverleyensis*, *Planolites* isp., *Cruziana* isp., and *Teichichnus* isp. Besides, vertical domichnia represented by *Skolithos* isp. and ?*Monocraterion* isp. are present. The analysed

trace fossil assemblage is typical of the archetypal *Cruziana* and partly *Skolithos* ichnofacies (sensu Seilacher, 1970). Some of beds contain abundant Orthidae brachiopods (*Orthis* spp. and *Orthonambonites* sp.). Clastic sedimentation was replaced by carbonate sedimentation toward the top of the formation. This negatively influenced preservation of the trace fossils, which have the highest preservation potential in heterolithic siltstone-sandstone deposits. Trace fossils and sedimentary structures recognised suggest deposition of sandy material on the middle and lower shoreface with a possible influence of storms (cf. Pemberton *et al.*, 2001).

Cocks, L. R. M. (2002): Geol Soc London, Spec Publ, 201: 37–46.

Drosner, M. L., Bottjer, D. J. (1986): J Sedim Petrol, 56: 558–559.

Pemberton, S. G., Spila, M., Pulham, A. J., Saunders T., MacEachern, J. A., Robbins, D., Sinclair, I. K. (2001): Geol Assoc Canada Short Course Vol, 15: pp. 344.

Seilacher, A. (1970): In: Crimes, T. P., Harper, J. C. (Eds.), Geol J, 3: 447–476

Trela, W. (2006): Przegląd Geologiczny, 54: 622–631.

# Mineralogical and textural study of manganese oxides and oxi-hydroxides in the Úrkút manganese ore deposit, Hungary

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During the Toarcian anoxic event manganese rich strata were deposited Europe-wide. One of the largest known manganese accumulations of this horizon is the Úrkút deposit (Bakony Mountains, Transdanubian Range (TR), Hungary). The formation of the TR was part of the evolution of the Mesozoic Tethys Ocean system. In the Triassic extensive carbonate platforms were formed (Dachstein Limestone Formation). In the Jurassic, the carbonate platforms were dissected by extensional tectonics and they became drowned. The limited extension of the intraplatform basins thus formed resulted in a strong lateral variation of Jurassic sedimentation in the TR (Galácz & Vörös, 1972). Accordingly, the Úrkút Manganese Ore Formation, with its 40 meter maximum thickness, is only of a few kms lateral extension. There are two types of ore in the Úrkút manganese deposit: carbonatic and oxidic. The geological section we studied in the mine represents a transition between these types: the several meters thick, well bedded, predominantly carbonate ore alternates with oxidic layers. The current research was focussed on the lowermost manganese-oxide-rich layers, not studied in detail so far. These layers, occurring immediately above the footwall of the section, show massive, macroscopically unlayered texture. The formation of these black ("oxidic") layers has been assumed to be the result of the postdiagenetic pyrite oxidation related remobilization of the manganese. However, details of that process have never been revealed, neither mineralogically, nor geochemically.

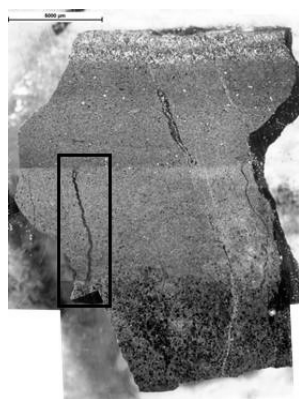


Fig. 1.: Oxidic manganese layer (oriented), consisting four different, mm-sized sublayers. The position of the veinlet shown in Fig. 2 is marked. Scale bar: 5 mm. Stereomicrograph.

Our aim was to map, down to the micrometer size range, the texture-related mineralogical features of these macroscopically homogeneous layers, in order to find potential traces of the prediagenetic, diagenetic and postdiagenetic processes at the boundary of the limestone footwall and the ore body. In our study we combined stereo and polarized reflected light microscopy, X-ray powder diffraction (XRD), scanning electron microscopy (SEM), X-ray microanalysis (SEM-EDX) and Raman-spectroscopy. It is the first time that oxidic manganese mineral phases, known before from bulk phase analyses only, can be connected to particular

microtextural features. From among the four mineral phases identified, cryptomelane and manganite dominate, while hollandite and a fourth phase, not identified till now, are present in subordinate amounts. Cryptomelane is fine-grained ( $\leq 1 \mu\text{m}$ ). Texturally it is present either as cavity filling matrix or as round-shaped aggregates/pellets?, up to 100–200  $\mu\text{m}$  in diameter, mostly around detrital mica crystals. As to manganite two different euhedral crystal generations could be distinguished. Few  $\mu\text{m}$  thin, 40–60  $\mu\text{m}$  wide platy manganite crystals form loose masses in separate sublayers (e.g. the uppermost sublayer in Fig. 1), or they are present as co-precipitates with cryptomelane in veinlets, syngenetic with the manganese oxide sublayer formation (Fig. 2). The other manganite generation, stubby crystals of around 50  $\mu\text{m}$ , fills post-sublayer-formation veins (e.g. the large vein crossing all sublayers in Fig. 1). Former works regarded manganite as "secondary, postgenetic" phase in the system. That matches our stubby crystal veins, but the textural position of the platy crystals needs additional explanation.

It is worth mentioning, that the two minerals (manganite and cryptomelane) represent not only two distinct species, but also two different oxidation states of manganese ( $\text{Mn}^{4+}$ ,  $\text{Mn}^{3+}$ ), suggesting that geochemical parameters might have changed during the formation of these manganese oxides at the bottom of the profile.

Pseudomorphic replacement of carbonate bioclasts by different oxidic manganese minerals was also observed (e.g. in the lowermost sublayer in Fig. 1). That process, being fabric-selective (preserving even the finest,  $\mu\text{m}$ -sized textural details of the fossils), must have been slow, probably not an aggressive dissolution-re-precipitation type one.

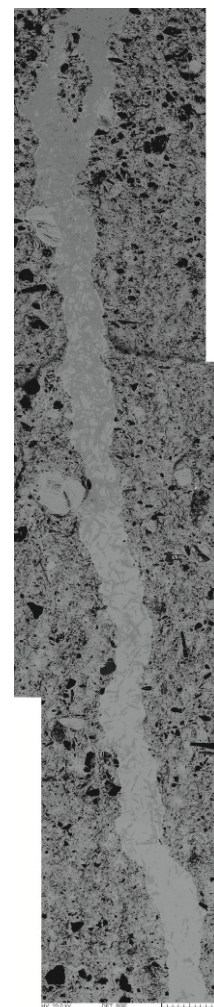
Detailed analysis of the texture and mineral composition of the oxidic sublayers, the replacement processes and the different veinlet generations show, that the formation of these massive bottom manganese oxide layers at the bottom of the deposit of Úrkút requires a more complex interpretation than it was suggested earlier.

Fig. 2. Details of the veinlet marked in Fig. 1.

From bottom up: pure massive cryptomelane (brighter matrix) changes gradually to manganite (darker laths and at the top – pure darker matrix).

The veinlet does not cross the sublayer border.

BSE image.



Galácz, A., Vörös, A. (1972): *Föld Közl.*, 102: 122–135.

## Sequence of deformation phases recorded in the low-grade metamorphic rocks of western Mt. Papuk (Croatia)

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Low-grade metamorphic rocks outcropping at the southwestern flanks of Mt. Papuk in Ravna Gora area belong to a Variscan crystalline complex called “Progressively Metamorphosed Complex” (Pamić & Lanphere, 1991). The studied samples are extremely interesting rocks due to complex microstructural relations, various types of developed foliations, pervasive folding, crenulation and cleavage. These rocks grade toward low- to medium-grade schists exposed in laterally more distant area toward the northwest where biotite, garnet and staurolite zones outcrop, grading eventually to migmatites.

In general, all samples show consistent mineral composition comprising chlorite, muscovite, quartz, feldspar, opaque minerals ( $\pm$  calcite) but with various microstructural features.

The complexity of relations between foliations is apparent in the samples from the outermost zone comprising three foliations (Fig. 1.).

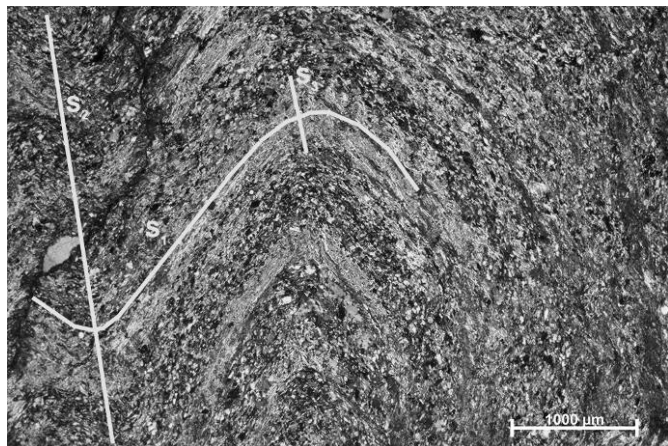


Fig. 1.: Primary foliation with distinctive muscovite-rich and quartz-rich domains containing developed secondary foliations, PPL, N+.

Thin sections are characterized by spaced foliation and two mineralogically distinct domains: muscovite-chlorite and quartz-feldspar-calcite. At the hinge points of highly folded muscovite-chlorite domains micro-folding is visible (Fig. 2.). Opaque minerals occur in both domains, but are slightly more concentrated within muscovite-chlorite domain. Calcite veins generally follow the main foliation and aggregates are also present, defined by larger polygonal crystals. Also, sample contains organic matter which occurs as thin layers parallel and oblique to the main foliation.

Further to the northwest samples display disjunctive foliation defined by chlorite-muscovite (cleavage domains) and quartz-feldspar-muscovite layers (microlithons). In the cleavage domains elongated fibrous (although somewhere clustered) chlorite occurs accompanied by fine-grained muscovite and thin calcite veins. Quartz grains dominate in microlithons showing a grain shape preferred orientation oblique to the foliation, but also minor amounts of feldspar, fine-grained muscovite and chlorite are present. Larger grains of dynamically recrystallised quartz with lack of preferred orientation form several aggregates throughout the

thin sections and those are usually surrounded by elongated fibrous chlorite. Opaque minerals are mostly associated with muscovite.

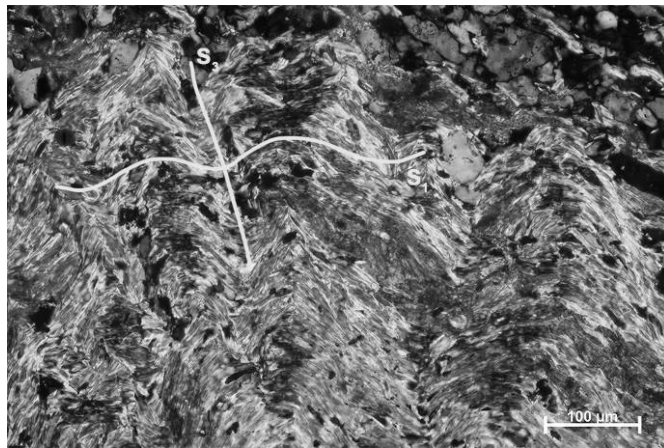


Fig. 2.: Well-formed micro-folding of muscovite-rich domain, PPL, N+.

The northernmost samples i.e. toward the higher grade zones in the field, display spaced foliation by which three main domains can be distinguished: muscovite-chlorite, quartz-feldspar-muscovite-chlorite and quartz-rich domains. Opaque minerals are evenly distributed through the thin sections, but slightly higher concentrations in muscovite-chlorite domains are noticeable. Muscovite-chlorite domains are characterized by distinctive crenulation cleavage and several larger sin- to post-kinematic chlorite crystals (Fig. 3.). Minerals in quartz-feldspar-muscovite-chlorite domains occur as equant fine-grained. The last domain is defined by dynamically recrystallised quartz aggregates and veins accompanied by clusters of large, fibrous chlorite.

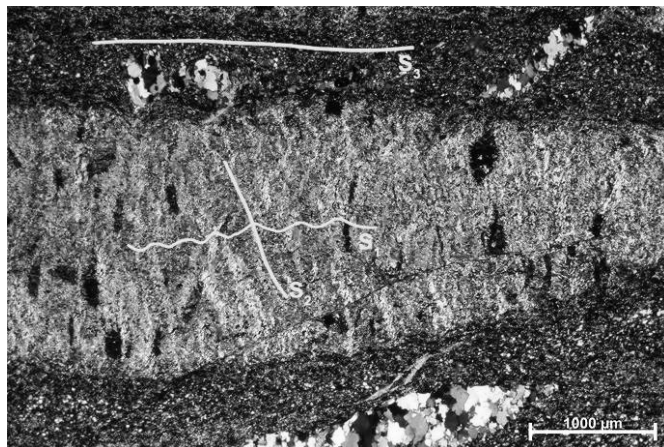


Fig. 3.: Sin- to post-kinematic chlorite grains developed within crenulated muscovite-chlorite domain, PPL, N+.

Observed foliation sequence has potential to be a marker of relative succession of regional geological events. Further research will be concentrated on the age dating of accessory minerals with exact position in respect to the foliations.

Pamić, J., Lanphere, M. (1991): Geol Ljubljana, 34: 81-253.

## Sarmatian ostracods from the Preutești area, Suceava County, Romania (Moldavian Platform)

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The studied area is situated in the north-western part of the Moldavian Plateau, within the basin of the Șomuzul Mare, a tributary of the Siret River (Fig. 1).

We have analysed 10 samples collected from the natural outcrops of the Logofătu, Gheorghe and Muscalu Brooks, more precisely from the sandy clay deposits that are part of the Arghira Member, Șomuz Formation (Ionesi, 2006).

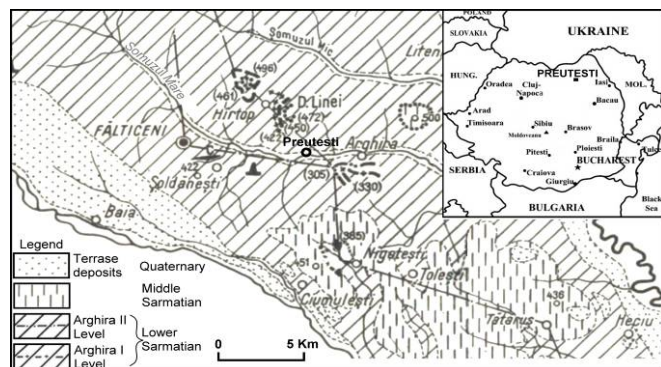


Fig. 1: The location of studied area (after Ionesi, 1968).

The ostracods of this area have been studied by Ionesi & Chintăuan (1978). The two authors described 20 ostracod taxa found in the outcrops of the Muscalu brook, in the sandy clay deposits between the levels Arghira I and Arghira II of the Arghira Member.

In the present study, 24 ostracod taxa have been identified. Among these, *Cyprideis pannonica* (Méhes, 1908), *Cyprideis mataschensis* Gross, (2008), *Bythocypris arcuata* (Münster, 1830), *Cyamocytheridea leptostigma leptostigma* (Reuss, 1850), *Loxoconcha minima* (Müller, 1894), *Leptocythere mironovi* (Schneider, 1939) are the most frequent.

A number of 18 taxa are mentioned for the first time in the area (table 1). The fauna was determined using the following works: Carbonnel G., (1969), Cernajsek T., (1974), Gross M., (2002), Ionesi & Chintăuan (1978), Müller, (1894) and Tóth, (2008).

No.	Taxa
1	<i>Amnicythère tenuis</i> (Reuss, 1850)
2	<i>Aurila (Euaurila) notata</i> (Reuss, 1850)
3	<i>Bythocypris arcuata</i> (Münster, 1830)
4	<i>Bythocypris pappi</i> Cernajsek, 1974
5	<i>Candona bitruncata</i> Carboneel, 1969
6	<i>Cyamocytheridea derii</i> (Zalányi, 1913)
7	<i>Cyamocytheridea leptostigma leptostigma</i> (Reuss, 1850)
8	<i>Cytheridea hungarica</i> Zalányi, 1913
9	<i>Cyprideis sublitoralis</i> Pokorný, 1952
10	<i>Cyprideis mataschensis</i> Gross, 2008
11	<i>Euxinocythere (Euxinocythere) praebosqueti</i> (Suzin, 1956)
12	<i>Fabaeformiscandona pokornyi</i> (Kheil, 1964)
13	<i>Henryhowella asperima</i> (Reuss, 1850)
14	<i>Loxocorniculum hastatum</i> (Reuss, 1850)
15	<i>Loxocorniculum schmidi</i> (Cernajsek, 1974)
16	<i>Miocyprideis janoscheki</i> Kollman, 1958
17	<i>Miocyprideis sarmatica</i> (Zalányi, 1913)
18	<i>Potamocypris gracilis</i> (Sieber, 1905)

Table 1: The ostracod taxa mentioned for the first time in samples collected from the outcrops of the Preutești area.

Carbonnel, G. (1969): Doc Lab Geol Fac Sci de Lyon: pp. 469. (in French)

Cernajsek, T. (1974): Chronostratigraphy and Neostatotype Miocene of the Central Paratethys IV: 458 – 491. (in German)

Gross, M. (2002): Midle Miocene ostracods from the Vienna Basin (Badenian/Sarmatian, Austria), Insitute of Geology and Paleontology of Karl-Franzens University of Graz, pp. 343. (in German)

Gross, M., Minati K., Danielopol D.L., Pillier W.E. (2008): Senckenbergiana lethaea, 88: 161-181.

Ionesi, B. (1968): The stratigraphy of Miocene platform deposits located between the valleys of the Siret and Moldova rivers, Ed Roman Acad, Bucharest, pp. 395. (in Romanian)

Ionesi, B., Chintăuan I. (1978): Ann Nat Sc Mus Piatra Neamț, Geol-Geogr Ser: 205 – 225. (in Romanian)

Ionesi, V. (2006): The Sarmatian between the valleys of the Siret and Șomuzul Mare rivers, Ed "Alexandru Ioan Cuza" Univ, Iași, pp. 237. (in Romanian)

Müller, G. W., (1894): Fauna and Flora of the Bay of Naples, Monographie I-VII: 1-404. (in German)

Tóth, E. (2008): Geol Pannon, 36: 101-151.



## Gold in "brown mud"

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My research focuses on high Au anomalies in brown earthy sediments detected by Avala Resources Ltd. along the western margin of the Timok Magmatic Complex (TMC) in the Republic of Serbia. Within the north-south oriented, 80-km-long TMC, there are four differently mineralized metallogenic belts progressing from east to west (Kolb *et al.*, 2012): a Cu-Au porphyry belt, a high sulphidation Au-Cu belt, a diorite porphyry Cu-Au belt, and a sedimentary rock-hosted auriferous belt on the western margin of the TMC. By stream sediment and soil sampling Avala Resources revealed several sedimentary rock-hosted gold deposits (SRHG) in a 20-km-long belt of anomalous Au-As-Sb-Hg-Tl mineralization. These newly discovered gold deposits are Bigar Hill, Korkan and Kraku Pester (van der Toorn *et al.*, 2013). The area of my interest, the Bigar Prospect, is located southeast of Bigar Hill. It covers an area of 0.7 km<sup>2</sup> along the contact between a western, marmorized Jurassic-Cretaceous limestone dominated area and an eastern calc-silicate dominated area. The reasons for the contact metamorphic effect are Late Cretaceous intrusive bodies (van der Toorn *et al.*, 2013). Three main fault systems dominate the wider area of the Bigar Prospect (van der Toorn *et al.*, 2013). The oldest system is composed of NW-SE striking structures; a younger is a NNE-SSW striking trend, and the youngest one is an E-W striking system of normal faults. These fault systems have probably been long-lived and have been re-activated several times. Gold mineralization exists both in NW-SE and in NNE-SSW trends but the E-W striking faults lack in it. These E-W striking post-mineralization normal faults have the potential to protect mineralized rocks from erosion by forming graben-like structures.

Geochemical analyses showed that gold is often enriched on limestone and calc-silicate dominated areas. Samples from these areas –both from exploration trenches on the surface and from drillcores– often have a dark-brown, earthy appearance, usually with high gold content (2-10 ppm Au). Due to their weathered appearance it is hard to define their origin. It is also unknown where their high Au, Ag, Pb, Zn and Mn content comes from and to what mineral phases they are connected. The goal of this study is to determine the exact location of gold in the brown earthy material and the nature of the gold concentrating processes.

To answer these questions, complex analytical methods have been used. Mud-like samples were sieved into six different grain size fractions. Each fraction was studied under stereomicroscope to see the appearance of the individual grains. The basic mineralogical composition of the samples (bulk and predominant grain size fractions) was determined by X-ray powder diffraction (XPD). Results of XPD analyses highlighted the connection between different samples, creating a possibility to group them by their mineralogical composition. SEM-EDX measurements were carried out on grain separates and polished sections. 19 samples were selected for ICP-MS and ICP-AAS analysis for 51 elements in the laboratory of SGS Serbia in Bor.

According to XPD results, brown, mud-like samples from drillcores are usually rich in goethite, kaolinite and smectite

minerals, have a moderate amount of feldspar and occasionally grossular. Similar, brown earthy samples from exploration trenches are rich in goethite, kaolinite, illite, chlorite, occasionally with high gypsum content and in some cases have moderate feldspar content. Carbonates and quartz are found both in drillcores and in exploration trenches.

The drillcore sample with the highest gold content contains a high amount of brown mud. Upon a closer look, this material can be further divided into three subparts, a creamy white, a rusty brown and a dark brown material. The creamy white part is composed of "detrital grains" in a clayey matrix. The detrital grains are grossular, K-feldspar, quartz, occasionally epidote and titanite, while the matrix is smectite. Kaolinite occurs in patches of distinct contour. Close to the border towards the rusty brown part, 500-µm-size radial groups of idiomorphic cerussite crystals were found. The rusty brown material consists of goethite pseudomorphs after cubic minerals, most probably pyrite. In some cases patchy Mn-Pb-Zn-enrichment is also associated with the pseudomorphs. The third, black part is a very porous, weakly compacted dust. According to the XPD analysis, it contains predominantly goethite. The mineral composition of this subsample is analogous to the highest gold-containing sample according to the observations done so far.

Sieving revealed that the brown mud-like samples are dominated by the <32 µm grain size fraction. This fraction is composed of goethite and clay minerals, such as smectites, kaolinite or illite. In the larger grain size fractions, the most frequent phases were bronze-brown to black, shiny, striated, cubic or cube-like goethite pseudomorphs after pyrite. Another frequent grain type is black, irregular, porous scoria-like clasts. According to SEM-EDX analyses these are likely to be Mn-Pb-Zn oxide or oxyhydroxide phases. These are present in brown muds and their overlying carbonates as well, filling intergranular spaces, cracks and pores, so probably they are the results of late epigenetic processes.

So far, the most valuable ore-related pieces of information from the brown muds seem to be the goethite pseudomorphs, the Mn-Fe-Zn precipitations and the surviving garnets which can be found both in brown muds and in fresh calc-silicate rocks. Therefore, I concentrated on the presence of sulphides and garnets in fresh rocks of calc-silicates –found both in drillcores and on the surface– to mark them as possible source rocks of the brown muds. SEM-EDX analyses revealed that in drillcore samples of fresh skarns, tabular and columnar minerals are replaced by iron-disulphides. Concerning garnets, they are present as andraditic grossulars in brown muds, while skarns in drillcores and on the surface host andradites and grossularic andradites. Based on these results, so far I did not find any direct evidence for a genetic connection between the brown muds and fresh skarns.

Kolb, M., von Quadt, A., Peytcheva, I., Heinrich, C.A., Fowler, S.J., Cvetkovic, V. (2013): *J Petrol*, 54/3: 421-451.

van der Toorn, J., Knaak, M., Tosdal, R., Davis, B., Hasson, S., (2013): 12<sup>th</sup> Biennial SGA Meeting, Mineral deposit research for a high-tech world, Uppsala, Sweden, 2: 691-694.

## Biostratigraphic Distribution of the Cretaceous Oysters (Bivalvia) in Volyno-Podolian region of East European Craton.

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The collection of oysters from Cretaceous sediments of southwest of the East European Platform was studied. The studied material was collected by S. Pasternak, V. Hawrylyshyn and others in the second half of the 20<sup>th</sup> century and housed in the State Museum of Natural History of National Academy of Science of Ukraine (Lviv).

The fauna of oysters irregularly distributed and presented by variable number of species and the remains almost in all stage age of Cretaceous (Table 1). High adaptability of oysters to variable of biotic and abiotic environmental conditions was displayed on the shell morphology. The shells variability related primarily to a change of depth and the nature of substrate. These indicators were fundamental to their development and distribution on the territory of studied region.

The sediments of Albian are composed of glauconitic sandstone with gravel and conglomerate, in the lower part it consists of the redeposition of concretions of ripheans phosphorite. The remains of *Amphidonta conica* were numerically dominated in the complex of Albian fauna. *Amphidonta laterali*, *A. sigmoidea*, *Gryphaostrea canaliculata*, *Rhynchostreon suborbiculatum* and *Arctostrea carinata* were presented by a smaller number of specimens. The investigated material consists of medium size valves (15-30mm). Morphological characteristics of shells pointed to shallow depth and warm climate in sea of the Late Albian.

The most abundant and diversified fauna of Cretaceous oysters comes from Cenomanian. The deposits of Cenomanian are consisting of chalky limestone concretions and nodules of black, gray and spotted marl, a sandy stratum and inoceramids limestone. Large number of determined oysters indicates enabling environment for their development in the coastal sandy facies. The new paleobiocenose composed by chalcedonic remains of *Amphidonta conica*. It formed the oyster banks on underwater humps and shallows of the Medium Prydnistrov'ya. The identified remains of *Amphidonta cf. reussi*, *A. conica*, *Amphidonta lateralis*, *A. sigmoidea*, *Gryphaostrea canaliculata* indicated conditions of Early Cenomanian of Volyn-Podolian basin did not differ from Late Albian.

The great development of Bivalvia took place at the boundary between the Early and Late Cenomanian. The general character structure of the features of oysters shells attested, that it lived in shallow, warm, moderate salinity water enriched in oxygen. The shells of *Hiotissa semiplana* tell about the reef nature of the Cenomanian biocenose.

At Turonian stage is composed of soft, white sandy chalk, varying degrees of siliceous limestone. The fauna of oysters were represented only by a small number of *Gryphaostrea canaliculata*, *Liostrea incurva*. The extinction of thermophiles, shallow oysters groups at Turonian pointed to temperature reduction, diminution of nutrient and small content of oxygen of the water environment.

At Coniacian stage the oysters were not found. Probably, a fauna of Inoceramidae which reached its peak, and formed immobile benthos on shallow water forced out the groups of oysters.

SPECIES	ALBIAN	CENOMAN	TURONIAN	CONIACIAN	SANTONIAN	CAMPANIA	MAASTRIC
<i>Amphidonta cf. reussi</i> (Netsch)	+	+					
<i>Amphidonta conica</i> (Sowerby)	+	+					
<i>Amphidonta haliatidea</i> (Sowerby)		+					
<i>Amphidonta lateralis</i> (Nilsson)	+	+					
<i>Amphidonta sigmoidea</i> (Reuss)	+	+					
<i>Arctostrea carinata</i> (Lamarck)	+	+					
<i>Arctostrea diluviana</i> (Linneaus)	+	+					
<i>Arctostrea</i> sp.		+					
<i>Ceratostreon</i> sp.		+					
<i>Gryphaea nikitini</i> (Arkhangelski)		+					
<i>Gryphaea vesicularis</i> (Lamarck)							+
<i>Gryphaostrea canaliculata</i> (Sowerby)	+	+	+				
<i>Hiotissa semiplana</i> (Sowerby)		+					
<i>Hiotissa</i> sp.							+
<i>Liostrea acutirostris</i> (Nilsson)		+					
<i>Liostrea boucheroni</i> (Coquand)					+	+	
<i>Liostrea cf. dagnasensis</i> Rengarten		+					
<i>Liostrea incurva</i> (Nilsson)			+		+	+	+
<i>Liostrea wegmaniana</i> (d'Orbigny)		+					
<i>Rhynchostreon suborbiculatum</i> (Lamarck)	+	+					

Table 1.: Stratigraphic Distribution of oysters in Cretaceous Sediments of Volyno-Podolian.

The taxonomic composition of oysters in Santonian was made up by numerous valves of *Liostrea boucheroni* and *Liostrea incurva*. It settled on aleuritic bottom. Shallow depth of sea, warm climate, clean water and a small amount of other fauna of molluscs formed favorable conditions for the existence of oysters.

The sediments of Campanian consist of sandstone with layers of sand, loamy sediment, siltstone and argillaceous limestone. At Campanian stage, rarely valves of *Liostrea boucheroni* and *Liostrea incurva* were identified.

In comparison with Campanian, the Maastrichtian stage was more saturated with oysters. The sediments of Maastrichtian consist of light and gray with a green tint, argillaceous limestone, marl, marly siltstone and sandstone. Among the fauna of oysters *Gryphaea vesicularis*, *Hiotissa* sp., *Liostrea acutirostris*, *Liostrea incurva* have been identified. Occurrence and stratigraphic position of massive valves of *Gryphaea vesicularis*, which constitute 63% the number of the oysters, tell about the deeper section of Volyno-Podolian Sea.

# The Paleocene assemblages of agglutinated foraminifera from deep-water deposits of the northern Tarcău Nappe (Eastern Carpathians, Romania)

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The studied section is situated in the northern part of the Tarcău Nappe, in the Eastern Carpathians Flysch (Fig. 1).

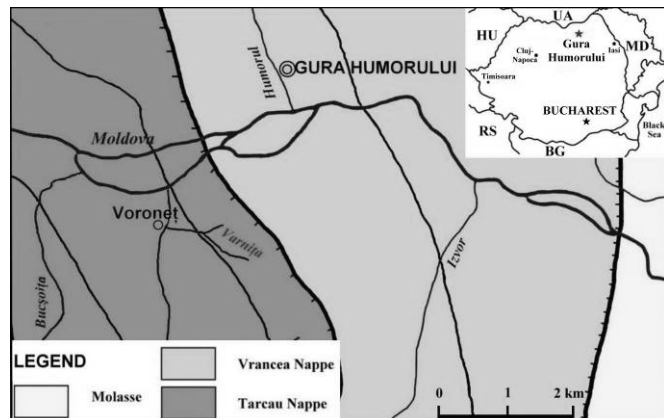


Fig. 1: Location of the investigated area (after Geological Map of Moldovița – Gura Humorului region; Ionesi, 1971).

We have analysed agglutinated foraminifera from clay deposits collected from Runcu (Ionesi, 1998) and Izvor (Ionesi, 1966) Formation on Varnița Brook, starting from its confluence with Voroneț Brook, which is a tributary of Moldova River.

In this area, previous studies on Paleogene microfauna were carried out by Ionesi and Tocorjescu (1968), and Ionesi (1971, 1975).

The microfaunal analyses were performed on 13 samples, 2 samples from Runcu Formation and 11 samples from Izvor Formation. We identified 30 taxa of agglutinated foraminifera, having a scattered distribution throughout the studied interval. In the foraminiferal assemblages, the species *Rhabdammina linearis* (Brady), *Saccammina placenta* (Grzybowski), *Saccammina complanata* (Franke), *Hyperammina rugosa* Vardenius and Van Hinte and *Kalamopsis grzybowskii* (Dylazanka) are dominant.

From a total of 30 taxa, what we have mentioned in this study, 8 are listed for the first time in this area (Table 1).

No.	Taxa	Runcu F.	Izvor F.
1	<i>Rhabdammina linearis</i> (Brady)	x	x
2	<i>Hyperammina rugosa</i> Vardenius and Van Hinte	x	x
3	<i>Ammodiscus peruvianus</i> Berry	x	
4	<i>Ammodiscus siliceus</i> Terquem	x	
5	<i>Trochamminoides trifolius</i> (Egger)		x
6	<i>Recurvoidella lamella</i> (Grzybowski)	x	x
7	<i>Recurvoides immane</i> (Grzybowski)	x	
8	<i>Recurvoides walteri</i> (Grzybowski)		x

Table 1: Foraminiferal taxa mentioned for the first time on Varnița Brook

Based on the presence of the index taxon *Rzehakina fissistomata* (Grzybowski), the age of the analysed foraminiferal assemblages was determined as being Paleocene (Bubik, 1995; Bąk *et al.*, 1997; Olszewska, 1997; Oszcypko *et al.*, 2005).

The foraminiferal assemblages consist of a diverse association of agglutinated foraminifera, belonging to the so called “Flysch-type” biofacies that suggest a bathyal to abyssal sedimentation paleoenvironment.

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## Impact analyses of earthquake in epicentral area of Kraljevo

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This paper presents the impact and consequences of the strongest earthquake in XXI century in Serbia, which happened in Kraljevo town on 3.11.2010. Otherwise, this area is one of the seismically active regions in Serbia

Kraljevo is a city in Republic of Serbia, located in the centre of the country (Fig. 1.). This area follows, chronologically speaking, very active seismicity.

For analyses of earthquake and its affection we shall take into account the date 03.11.2010., when an intense tremor magnitude 5.4 of Richter scale occurred. Figure 2. shows the map of Serbia with places marked where earthquakes have happened.



Fig. 1.: Map of Serbia, the area of the observations are marked with black

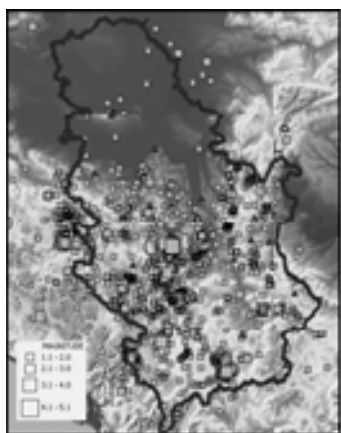


Fig. 2: Map of earthquakes in Serbia (dark grey triangles are seismological stations, while the gray squares marks the value of magnitude of the earthquakes happened in 2010)

After the main earthquake in epicentral area in Kraljevo, its effects in the soil were also observed. In Sira village, a long crack has appeared, longer than 20m (see Fig. 3., marked as number 1.) from which it has expired warm gray-black sand. In the same location (see Fig. 3., marked as number 4.) in the spa of Siran, one of the wellheads has increased munificence five to six times. Enhanced concentration of sulfur was observed in the water which returned to the previous concentration within two days.

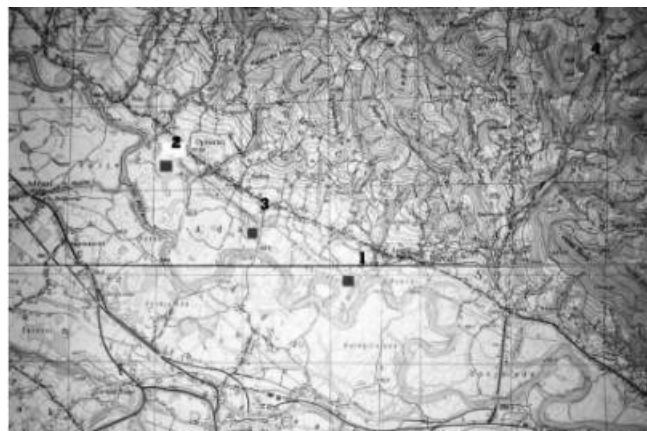


Fig. 3: Locations of appearance of liquefaction in the epicentral area of the earthquake

Nearby, at Oplakic place (Fig 3., marked as number 2.), a crack was also observed, 4-5 m long, from which also warm gray-black sand expired. In Sira, in one well (Fig 3., marked as number 3.), in which the water level was on a depth of 5m, has thrown water and the well was filled in with sand.

These phenomena of seismic deformation in soil are possible consequences of the earthquake and they are classified in four categories:

1. Hydrological effects: level changes of water in wells, waves on water surfaces, changes of capacity of wellhead
2. Effects of slope instability: attrition, small landslides, smaller rockfalls, landslides and massive rockfalls;
3. Horizontal processes in the soil: little and big cracks in soil;
4. Convergent processes or complicated cases: landslides, liquefaction.

Earthquakes are the major natural hazards that lead to loss of life and economic losses due to damage of the buildings. The low quality of old masonry constructions represents a significant hazard in areas of high seismic hazard on the territory of Serbia and studies of the risk of earthquakes is necessary, as well as to develop a correlation between the intensity of the earthquake and extent of damage to buildings in an area or to define vulnerability of buildings to the effects of the earthquake and funds needed for reconstruction. Citizens often want to settle on places which can be easily affected by some hazard. However, it is much more damage, if the settlements built in places that are constantly under the threat of disaster that may cause tremendous damage, such as, for example, earthquakes.

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<http://www.seismo.gov.rs/Seizmicnost/Aktuelna.htm>  
<http://www.seismo.gov.rs/Vesti/analiza.pdf>

## Devonian brachiopod shales of the Grzegorzowice-Skały section (Holy Cross Mountains, Central Poland): the attempt of paleoenvironment reconstruction

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The Holy Cross Mountains (HCM) is one of the most significant geological heritage sites in the European continent. This mountain range located in central Poland and it is a part of a larger structure called 'Mid-Polish Anticlinorium' (Żelaźniewicz *et al.*, 2011). Central part of the HCM called Palaeozoic core is one of the oldest mountain ranges in Europe. Historical geodiversity of the region is evident through the sedimentary rocks which represent every period beginning from the Cambrian. The only exception is the Paleogene period, presumably occurring in karst forms but has not yet been proven (Urban, 2008). Cambrian and Devonian rock occupy most of the Palaeozoic core of the HCM area. Because of the lithological formation, which is the basis of carbonate and quartz materials, the Devonian system of the HCM constantly aroused great interest (Urban, 2008).

The Early to Middle Devonian rock sequence crops out at the slopes of Dobručna creek valley at about 3.5 km distance, in the outcrops. The Lower Devonian shallow marine and the occasional terrestrial deposits of the siliclastic-clayey rocks were replaced by the carbonate succession which encompasses in the beginning of the Middle Devonian. Grzegorzowice-Skały section is located about 8 km NE of Nowa Słupia. The section represents formations from the Upper Emsian to the Lower Givetian stages. Grzegorzowice-Skały profile (stratotype) is represented by marine sandstones, shales, marls, limestone and dolostone with conodonts, corals, crinoids, brachiopods, ostracods, trilobites and acritarchs Pajchłowa (1957).

This geological site is located outside of the western wall of the limestone and dolomite quarry called "Skały". The fossil assemblage of this section was precisely studied by Pajchłowa (1957). She gave detailed description of the entire section and identified a number of fossil species. Some of them were revised and allocated to other genera. So far, the trials of the paleoenvironment reconstructions have not been undertaken.

The outcrop causing the shales and marls is rich in well preserved fossils. Various specimens of brachiopods (*Schizophoria resupinata*, *Schizophoria schnuri*, *Eleutherokomma diluvianoides*,

*Xystostrophia umbraculum*, *Primpilaria primpilaris*, *Leptaena analogaeformis*, *Poloniproductus varians*, *Atrypa depressa*), individual corals such as *Calceola sandalina* and *Zaphrentis* sp., Crinoids and uncommon trilobites like *Phacops schloteimi* can be found there. In the outcrop these fossils can often be occurred in nests accumulations.

Numerous and diverse brachiopods occurred in so-called "brachiopod shales", which are in fact horizontally laminated siltstones. Their amount and diversity as well as based on the sediment features let us conclude that a lot of organisms adapted to living on the surface of muddy substrate. A non-bioturbated sediment with primary sedimentary structures signify that there was no infaunalization in general. Rugose corals are one of the exceptions to this extent. A significant amount of brachiopods have shell plane with spines that help them to stay on the surface of the soft sediment. Within the common genus of brachiopods we usually observe only single species and from this we can assume that mostly opportunistic species are present. The muddy deposits lie generally within carbonate series and this suggests different sedimentation conditions of "brachiopod shales", which were probably deposited in some isolated lagoon with terrigenous material alimentation.

The preliminary results indicate that the outcrop mentioned and its fossils are well-known but they need a new taxonomical classification and an attempt of paleoenvironment reconstruction for these selected shales. The poster deals with only a necessity of the scrupulous analysis and it notices the initial observations.

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# Neotectonic and recent fault activity in NE Croatia: evidences from DEM based morphometry, structural analysis of 2D seismic sections and 2D GPR mapping

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Relief is often classified as polyphasic phenomena, which shows multiple tectonic overprints and produces unique physiographic characteristics of the certain part of Earth's surface. Analysis of three-dimensional properties and origin of landscape often implies multidisciplinary quantitative approach connecting active tectonic processes with climate and erosion features through available data from field of geology, seismology, geochronology and tectonic geomorphology, etc. In this work, identification of neotectonic and recent active faults in Bilogora Mt. of NE Croatia was performed by combined DEM based morphometric analysis and structural analysis of 2D seismic sections, supplemented by 2D mapping with GPR.

Bilogora Mt. area is a Pliocene-Quaternary transpressional morphostructure or a positive flower structure (Prelogović *et al.*, 1998) genetically linked with the tectonic evolution of the Drava depression and its SW prolongation (Bjelovar sub-depression). According to our data, this structure is related to the tectonic inversion of the NW-striking Drava Basin Boundary Fault (DBBF), which is an initially normal fault, which later turned into dextral strike-slip fault. Bilogora Mt. area is predominantly composed of highly deformed clastic Pliocene-Quaternary sediments of the 3<sup>rd</sup> depositional megacycle of the SW Pannonian Basin in Croatia (Velić *et al.*, 2002; Saftić *et al.*, 2003). Recent tectonic activity in the area is confirmed by moderate seismicity (VI°-VIII° MCS,  $3.5 \leq M_L \leq 5.6$ ). Fault plane solutions in the northwestern part indicate NE-SW directed  $S_{hmax}$  and NE- to S-SW-dipping seismogenic structures characterized by strike-slip and reverse motions (Herak *et al.*, 2009).

Computer-based morphometry using DEM (10m resolution) was performed by ESRI ArcMap 9.3.1. software with available extensions (CalHypso, Spatial Analyst, ArcHydro 1.1 and StPro.) and Matlab software. Study area, divided into 131 drainage basins, was analysed by relief and basin morphometry (elevation and slope distribution, hypsometry, asymmetry factor), and longitudinal stream profile morphometry (maximal concavity, distance from the source, concavity factor, steepness index, and concavity index). Morphometry results points to several drainage basins affected by recent on-going tectonics. These drainage basins and streams are located: i) between towns of Koprivnica and Pitomača in the NW part, and ii) between towns of Virovitica and Daruvar in SE part. Furthermore on-going tectonics was cross-checked by a set of 2D

seismic sections and boreholes using Schlumberger Petrel Seismic to Simulation software. As a result, 3D structural depth model was constructed, with 6 stratigraphic horizons and fault planes active during the Neogene and Quaternary times. Morphometrically recognized on-going tectonics in the NW part of Bilogora Mt. area correlate well with subsurface fault-related folds formed in hangingwalls of normal-inverted and newly formed reverse faults, displacing the base Pliocene-Quaternary horizon and propagating towards the surface. Pliocene and Quaternary vertical offset along these faults varies between 20 and 490 m, indicating slip rate of 0.1 mm/year. By application of empirical geometrical fault-scaling, relationships of Wells & Coppersmith (1994), we estimate that some of the analysed faults could generate earthquakes with magnitudes up to 6.86, which are greater, than historically reported. The same faults could generate maximal vertical surface displacement < 1.46 m per seismic event.

Landscape response to ongoing tectonic activity was additionally studied by 2D mapping with Malá ProEx Georadar (RTA antenna with 50 MHz) at 6 selected locations. At three locations in the NW part, a vertical offset of very shallow stratigraphic horizons are confirmed to reach 0.5 m and the most recent tectonic activity by even surface-breaking faults was also confirmed.

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## Seismic interpretation of Neogene sediments; Jászság Basin, Hungary

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The Pannonian Basin is a back arc lake basin, surrounded by the belts of the Eastern Alps, Carpathians and Dinarides. The sub-basins of the Pannonian Basin are filled by varying thickness Neogene sedimentary rocks. These strata usually overlie the pre-Neogene basement with an erosional unconformity. My study area lies in the eastern Pannonian Basin, (Jászság sub-basin). The deposition of Upper Miocene sediments were characterized by sediment input from north-east (paleo-Tisa direction) and north-west (paleo-Danube direction) (Pogácsás, 1984). The deltaic systems were prograded southward direction and progressively filled the Lake Pannon between 11.6-2.6 Ma (Juhász *et al.*, 2007). The age of the basin fill sediments varies (from Middle Miocene to Pliocene), the Neogene sedimentation was controlled by the different intensity of the Neogene subsidence (Pogácsás, 1984).

This work based on partly 3D, partly 2D seismic data of the Jászság Basin, Kunmadaras area. The aim was to identify the Late Miocene depositional environments that range from the deep-water basin plain, slope, delta front to alluvial plain. The seismic interpretation was integrated with well- and core-logs.

The mapping was undertaken at different stratigraphic levels on the 3D dataset. Seismic attribute extractions were generated to illustrate the environments, geometries. Spectral decomposition maps (Fig. 1.) were constructed too, to identify meandering channels, channel-leave systems, mass flows. The most prominent identified features are the submarine channels cutting into the slope and into the previously deposited toe of slope deep-water sediments. This imaging method helped a lot to interpret and to understand the details of the subsurface stratigraphic architecture.

The Late-Neogene basement of the Kunmadaras area is becoming shallower from northwest to southeast because the late uplift of the south-southeast part of the study area. The thick Upper Miocene sedimentary succession is built up by various strata from deep lacustrine to fluvio-deltaic facies. The lower part of the deep-water basinal succession is mostly characterized by hemipelagic marls, while above it deep-water turbiditic sands can be found. The turbidites system are characterised by channels and submarine slumps (Fig. 1.) which can be seen fairly well on the spectral decomposition maps and amplitude maps. The slumping was probably caused by tectonic activity along a wrench fault zone resulting in the failure of loosely packed sediments on the slope (Juhász *et al.*, 2013). The uppermost part of the deep-lacustrine succession consists of mostly slope marls, siltstones which are widespread throughout the study area. On section view we can recognize the slope by its sigmoidal to oblique reflections pattern.

The sediment of the slope are overlain by upward coarsening shoreface and deltafront facies. Delta plain sediments are thinner than the other facies in the study area. The delta plain sediments are overlain by thick alluvial deposits, mainly clays and silts with thinner and thicker sand beds. On the maps of the alluvial plain facies rivers channels seem to be appearing, although the individual river channels are not drawn out as sharply as the well developed feeder channels of the deep-water to of slope environment.

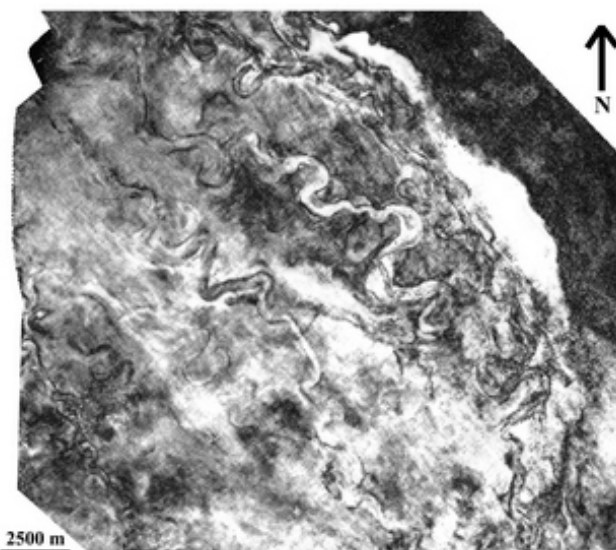


Fig. 1.: Spectral decomposition map constructed by Discrete Fourier Transform (DFT) to identify deep-water channel-leave complexes (around 1300 ms TWT)

A very specific feature of the study area is the meeting of two major sediment systems characterised by different input. It is assumed that initially the north-north east source direction was dominant because of the larger thickness of the sediments on the north-northeast. Subsequently the main sediment input come from north-northwest direction, which again was replaced by the dominance of northeast sediment input direction again.

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## Burrowing activity of macrofauna in recent meandering river sediments (Dunajec River, SE Poland)

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Riverine ecosystem is a particular place for interactions of biosphere with the deposited sediment. It is characterized by large energy gradients in relatively short time, and therefore forces on its habitants special adaptation, recorded in bioturbation structures. For predators there are mainly residential burrows (ichnologically interpreted as *Domichnia*), and for saprofares (especially earthworms) foraging trails (*Fodinichnia*). Understanding the relationships between organisms and the environment is an important prerequisite for understanding the functioning of modern and ancient flowing-water ecosystems.

It has been observed that in subsurface layers of natural levee, horizontally burrows of earthworms predominate. Vertical burrows of large earthworms, formed during a long period between two flooding events reaching over 2 m depth into the soil profile. Earthworms were often found in the vicinity of the European mole burrows, as well as along live and dead roots, going down with them in the deeper part of the sediment profile.

Observations of area surrounding our study reach has shown that fertile deposits of older terraces formed with many long-term interruptions in sedimentation processes, have a well-developed soil levels, more vulnerable to penetration than recently deposited sediments. In addition, older terrace deposits have completely disturbed layer boundaries by bioturbation processes and additionally characterized by a large degree of mixing in the individual layers. This is probably a result of moving up and down the fertile sediment by organisms, as well as mechanical leaching the sediment into the lower layers during subsequent floods or rainfalls. Such leaching processes can occur in a larger scale through the open burrows.

Sediments filling oxbow lakes are in the geological time scale very fast bioturbated and mixed by organisms which cause rapid penetration by blurring older by younger. On the scale of a few thousand years the final result is completely mixed sequence with visible bioturbation structures not older than a few decades. We are trying to compare such recent sediments, which deposited by the Dunajec River forming the nearby Pleistocene plains of higher terraces, built of river sands passing in eolian sands, locally with ferruginous nodules.

Bioturbation structures are not very abundant in the alluvial sediments. It is commonly recorded in the sediments of meandering systems than braided, especially in soil and subsoil layers. Such situation reflects better conditions to preserve the living activity traces in oxbow lakes and flood plains. In many cases there are thick sediment sequences without any bioturbation structures or with those restricted to certain layers. Distribution of organisms' penetration in the sediment is characterized as a function of the rate of sedimentation, energy of the environment and the amount of time between successive depositional episodes.

Active fluvial channels are known to be a medium or relatively high energy zones with rapid changes in the rate of sedimentation and erosion and coarse grain contrasting to the sediments deposited

in the neighbouring communities. Therefore, active channels represent stress environment for many organisms that makes the production and/or preservation of biogenic structures much more difficult. Burrows of fauna in the active fluvial channels are characterized by poorly differentiated sets of simple vertical penetration and escape traces.

In 2009-2012, on part of the study area (Dunajec valley in its lower course), we made some studies on the characteristics of ground beetle burrows (*Carabidae* family) and demonstrated their similarity to the ichnogenus *Macanopsis* known from continental deposits (Mikuś & Uchman, 2013a). It has also been proven an important role of flooding as an important factor controlling occurrence and distribution of fauna in the vertical horizontal alluvial deposits profile (Mikuś & Uchman, 2013b).

Although the typical geological literature is poor in the description of bioturbation structures of insects whose burrows are very numerous in sediment, entomological literature is a substantial set of knowledge about the biology, appearance of the burrows and environmental significance of this group. In addition to earthworms, our study area is rich in a large variety of fauna producing bioturbation structures, including centipedes (*Myriapoda*), a large group of beetles belonging to the ground beetles family (*Carabidae*), and the larvae of flying insects of the order *Diptera*, adults of the order *Hymenoptera* including *Andrenidae*.

The most common burrowing mammals are: European mole (*Talpa europaea*), fox (*Vulpes vulpes*), beaver (*Castor fiber*), shrews (*Soricidae*), European otter (*Lutra lutra*), several species of mice (*Muridae*) and voles (*Myodae*, *Microtae*). Special place in this species list occupies the only bird digging deep burrows in the natural levee sediments - swallow sand martin (*Riparia riparia*).

Among the amphibians, that would leave visible tropes on the floodplain sediment surface, here can be often found the gray toad (*Bufo bufo*), the water frog (*Rana esculenta*) and the common frog (*Rana temporaria*). Track mosaic on the surface of sediment supplements the footprints of birds: mallard duck (*Anas platyrhynchos*), terns (*Sterna hirundo*), black-headed gulls (*Larus ridibundus*), common gull (*Larus canus*), partridge (*Perdix perdix*), pheasant (*Phasianus colchicus*), white stork (*Ciconia ciconia*) and many other smaller species.

Such studies, involving impact of investigated organisms on recent alluvial sediment have not been carried out yet in relation to several different river environments. Knowledge about the bioturbation rate and grade also remains incomplete. Conducting each stage of the researches with adequate order and having appropriate geological knowledge, this project will significantly contribute to a better understanding of the burrowing behaviour and impact of fauna on alluvia deposited in recent riverine systems. This is also of great importance for the progress of sedimentology of river paleoenvironments.

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## Chronological analysis of earthquakes in the region of Kolubara

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This work represents chronological happening of earthquakes and consequences in the region of Kolubara, as one of the marked seismic places in Serbia. The period between 1998 and 2013 was analysed.

An earthquake is the result of a sudden release of energy in the crust of the Earth that creates seismic waves. The seismic activity of an area refers to the frequency, type and size of earthquakes experiences over period of time. Earthquakes are measured in seismological stations. Each seismological station recorded ground motions from seismometers.

Serbia does not represent an area of high seismic activity, but earthquake there have magnitude up to 5.8 Richter scale. Based on their energy, these earthquakes can be destructive. Serbia belongs to seismically active area, to the border of Mediterranean-trans-Asiatic earthquake zone, precisely the Mediterranean belt. Due to its position, it is on the edge of the plate, earthquakes in Serbia cannot be stronger than 6.2-6.3 Richter scale, according to seismologists. Seismic areas in Serbia are: Kopaonik, Rudnik, Krupanj, Maljen, Lazarevac, Svilajnac, Golubac, Vranje, Kraljevo and Urosevac-Gnjilane area. These earthquakes mark, by their position, the most important seismic zones in Serbia. The seismic area analysed in this work is Maljen's area with Kolubara region and the following municipalities: Valjevo, Osecina, Ub, Mionica and Ljig (presented in Fig. 1.). The area of the analysed region totals  $P = 2474 \text{ km}^2$ .

In the analysed area one of the strongest earthquakes in Serbia happened at the end of 20<sup>th</sup> century. This earthquake happened at midnight on 30<sup>th</sup> September, 1998. and the epicenter of 5.7 Richter scale was in Mionica region. Seismic waves of the earthquake at Mionica were registered by stations on over 10000km away. In Valjevo, the intensity of the earthquake at Mionica was VI degrees and in Mionica VIII degrees of Mercalli intensity scale. The same earthquake in Belgrade was V degrees and in Hungary II degrees of Mercalli scale as presented in Fig. 2.

The consequences of that earthquake were several weaker earthquakes in the next few months. Therefore in morning of April 30<sup>th</sup>, 1999, one of the strongest earthquakes happened in Mionica, with a magnitude of 5.4 Richter scale or VII degrees of Mercalli scale. Thereafter in chronology of earthquakes in the analysed area the magnitude and frequency of the earthquakes decreased as shown in Fig. 3. Only since 2006 their activity was gradually intensified and escalated in the period from 2009 to 2011, where stronger earthquakes happened. And from 2012 until August 20<sup>th</sup>, 2013, the seismic activity significantly decreased (as shown in Figs. 4-6.).

Well-known assumptions about the genesis of the earthquakes in Kolubara region are assumptions that claim that reasons for seismic activity are related to:

- Deep faults as old weakened zone
- Unequal speed of modern-day differential vertical movements
- Movements of tectonic plates, since Kolubara region lies on intersection of these plates

- The fact that Mionica, where the strongest seismic activity has been measured, lies on thermal water sources.

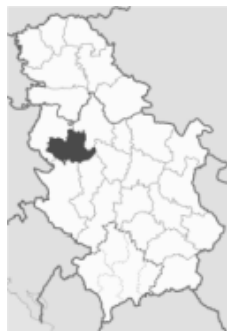


Fig. 1.: Kolubara county

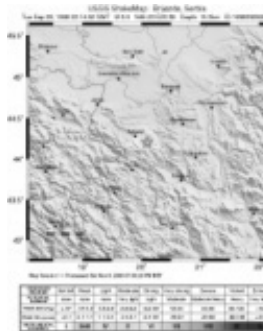


Fig. 2.: Earthquake in Mionica 1998

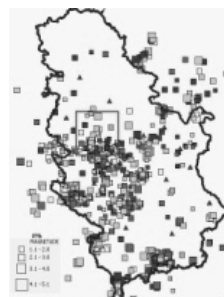


Fig. 3.: 2000-2005

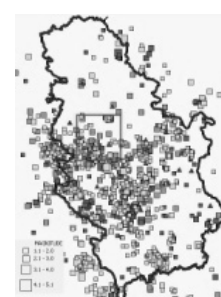


Fig. 4.: 2006-2008

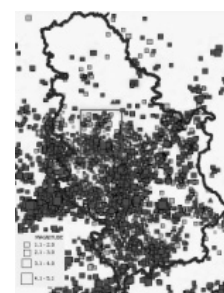


Fig. 5.: 2009-2011

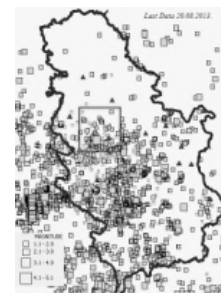


Fig. 6.: 2012-2013

The main goal of this work was to draw the attention of scientific audience to seismically active areas as high risk places, which could, due to reasons mentioned above, cause the appearance of the frequent earthquakes of different magnitudes. For that reason, it is necessary to make better informational systems with database with information about area and built environment (GIS) for the total management of seismic risk and risk of other natural disasters, as well as seismotectonic map of Serbia with active faults where the earthquakes are expected. This map would be used as base for making seismic hazard map, which predicts epicenters and magnitudes of earthquakes in longer time period.

All figures are taken from: <http://www.seismo.gov.rs/>



## Host rock elastic parameters and their relationships with ore location at the uranium deposit in granites

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The Antei vein stockwork uranium deposit is located within the granitic basement of the Sterlitsovskaya Caldera in NE Transbaikalia. The deposit consists of steep ore bodies confined to the branches of the Central fault zone trending with a wide (up to several tens of meters) area of dynamic influence (Laverov *et al.*, 2008). The Antei deposit is dissected by the deep fault No 13, with offshooting ore bodies located in the hanging wall. Studies were conducted on mining levels 9, 10, 11, 12, and 13 located at depths of ~ 550, 610, 670, 730 and 790 m from the surface, respectively. The host granitic rocks were sampled on each level.

We studied the elastic properties of rocks; velocities of compression ( $V_p$ ) and shear ( $V_s$ ) waves in dry and saturated states of rocks. Oriented samples were cubes with edges at least 50 mm long. The used equipment complex consists of generator - receiver ultrasonic signals «Panamatrix RR5072» (USA) and a pair of emitters P- and S- waves «Panamatrix» with operating frequency of 1 MHz. The resulting wave pattern was digitized using an oscilloscope «TieRie508» (Netherlands). Polysaccharide gel was used as a contact lubricant. Wave velocity measured in the dry state after drying at 70°C for 4 hours, and after 7 days of stepwise saturation by water. Practice shows that this method leads to full saturation of low porosity rock samples in contrast to the forced vacuum saturation by water. Error in determining the  $V_p$  and  $V_s$  after calibration on reference samples of quartz and steel did not exceed 1 % (Petrov *et al.*, 2011; Minaev *et al.*, 2013).

By measuring the velocities of  $V_p$  and  $V_s$  for the investigated core samples, the elastic moduli were calculated: K - the bulk modulus, GPa; G - shear modulus, GPa; E - Young's modulus, GPa and Poisson's ratio.

The values of all the parameters with calculation of standard deviation were adjusted to an average over the level. Graphs were constructed for each of the parameters. An example of these graphs is shown on Fig. 1.

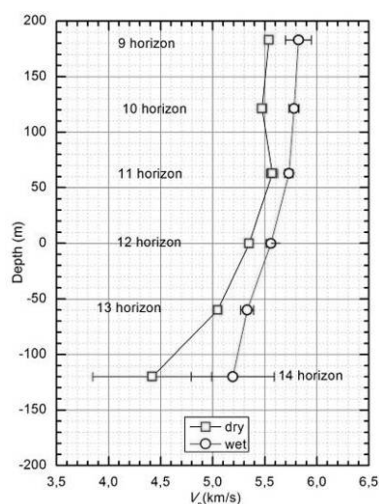


Fig. 1.: Variations of P-wave velocities in dry and wet conditions with depth.

All findings, what we can see on the graphs, suggest that with effect from 12<sup>th</sup> level the mechanical properties of the host rocks are deteriorate - they become brittle, porous and fractured. All this could create favorable conditions for circulation of ore-bearing solutions and ore location. In accordance with that the number of ore bodies and ore grade should increase with depth. In fact, we observe opposite situation – the ore bodies are becoming less and their power is reduced with the depth. What is the reason for this contradiction? The following hypotheses were constructed by the authors:

1. Preliminary calculations of the main values of the normal stress for the rock mass (not supported yet by instrumentally established parameters) shows that in the deep levels (level 12 and below) the dextral shear faulting regime changes to normal faulting regime with strike-slip component.

2. This normal faulting regime is realized along the fault No 13, plane and in the hanging wall within the network of ore-bearing small faults and fractures. The main intersection point of the fault No 13, and the ore faults is located near the level 12. Here all the petrophysical properties of the wall rocks are decreased with depth as probably result of tectonic stress impact on the fault knot.

3. As a result of multiple tectonothermal events, the fault knot could create an environment preferable for circulating meteoric waters and their mixing with hydrothermal ore-bearing solutions in particular down to the level 12. In this regard, a need for drilling directional wells in order to undercut the hidden uranium mineralization at the depth of the deposit is suggested.

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**(U-Th)/He geochronology of the Late Pleistocene dacite of the Csomád (Ciomadul) volcano (South-East Carpathians)**Kata Molnár<sup>1</sup>, Szabolcs Harangi<sup>2</sup>, István Dunkl<sup>3</sup>, Réka Lukács<sup>2</sup>, Axel K. Schmitt<sup>4</sup>, Balázs Kiss<sup>2</sup><sup>1</sup>Eötvös Loránd University, Budapest, Hungary<sup>2</sup>MTA-ELTE Volcanology Research Group, Göttingen, Germany<sup>4</sup>University of California, Los Angeles, USA

In the last few years the number of geological researches using the (U-Th)/He geochronology has significantly increased. This method is able to calculate the cooling age of various geological formations. The principle of the method is the accumulation of <sup>4</sup>He from U and Th decay after the mineral reaches a so called closure temperature (or partial retention zone). This temperature value is defined for each and every mineral which contains U and Th (e.g., zircon, apatite, and titanite). Even a complex evolution history can be set up in a certain geological environment with dating the different minerals with different closure temperature values in a slowly cooled rock body. The other application of the (U-Th)/He-geochronology is in case of rapidly cooled rocks on the Earth's surface (e.g., volcanic rocks) where demonstration of quantitative retention at ~25°C is sufficient to successfully apply He dating (Farley, 2002). The importance of defining this eruption age in case of volcanoes is due to the significance age difference between the crystallization age of minerals (e.g., U-Pb or U-Th geochronology of zircon crystals) and the eruption age of the volcano. The (U-Th)/He method assumes zero initial <sup>4</sup>He in the crystal and secular equilibrium among all daughters in the decay chain, a condition guaranteed for crystals formed more than ~350 kyr prior to the onset of He accumulation. For most applications the second assumption is valid but in case of younger eruptions the effects of secular disequilibrium must be considered and He ages must be corrected considering the results of <sup>230</sup>Th/<sup>238</sup>U dating (Schmitt, 2011).

In the Carpathian-Pannonian Region the youngest volcanic activities occurred at the Csomád (Ciomadul) volcano which is the southernmost eruptive center along the Kelemen-Görgény-Hargita (Calimani-Gurghui-Harghita) volcanic chain. The ages of the eruptions which were dated previously with different methods (e.g., K/Ar, Ar/Ar <sup>14</sup>C) vary in a wide range (from 30 kyr to ~600 kyr; Pécskay *et al.*, 1995, Karátson, 2007, Harangi *et al.*, 2010). In this

study the samples were collected from several outcrops of the volcanic complex, pumices and lava dome rocks, as well. The aim was to get a certainty about the applicability of the combined <sup>230</sup>Th/<sup>238</sup>U and (U-Th)/He dating of zircon. In case of two outcrops (Sepsibükszád/Bixad and Tusnádfürdő/Baile Tusnad) radiocarbon ages were available dated on charcoal fragments (Harangi *et al.*, 2010). Therefore these samples are suitable for testing the applicability of the combined <sup>230</sup>Th/<sup>238</sup>U and (U-Th)/He method. In case of the other samples we provide uncorrected zircon (U-Th)/He ages.

The uncorrected zircon He-ages imply that the period of volcanic activity of the Csomád (Ciomadul) volcano is much younger (30-250 kyr) than it was thought based on the previous geochronological data. Data correction using U-series dating will modify the present ages with maximum few thousand years. In case of the samples from Sepsibükszád (Bixad) and Tusnádfürdő (Baile Tusnad) the <sup>14</sup>C-ages gave 31.5+/-0.26 kyr and 42.3+/-1 kyr, respectively. The combined <sup>230</sup>Th/<sup>238</sup>U and (U-Th)/He ages on zircon gave the same ages within the error (31.9+/-3.3 kyr and 46.6+/-3.7 kyr, respectively). These results confirmed the young ages of the formations and revealed the applicability of this combined method in case of the Csomád (Ciomadul) volcano.

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# Study of Late Miocene-Early Pliocene evolution of the Dráva Basin, based on spectral decomposition and well log correlation

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The Dráva Basin is the south-western sub-basin of the Neogene-Quaternary Pannonian Basin. The Late Miocene sedimentary succession of the Dráva Basin is built up by deposits of the Lake Pannon which indicated gradually decrease of salinity. The prograding shelf margin reached the Dráva Basin before 6.8 Ma (Magyar, 2013). Late Miocene inversion of the basin generated a major unconformity (Magyar & Sztanó, 2008) at the boundary of alluvial and shelf formations. This significant surface is characterized by onlapping reflectors terminated on the unconformity itself (Pogácsás, 1984).

The sediment infilling process of the Dráva Basin was reconstructed by stratigraphic and facies interpretation of a 12x17 km 3D seismic survey and logs from five wells. Dozens of seismic events were correlated and mapped. Amplitude maps for each horizon picked on constant phase were performed as well.

Due to the basin inversion, flattening the 3D seismic data was needed to identify the slope related horizons. Selecting the flattened horizon was based on restoring the conditions at the time of deposition.

In the Dráva Basin the southeastward migrating shelf margin was formed by aggradational and progradational clinothems. Determination of these clinothems was necessary in order to understand their migration path. Aggradational clinothems are characterized by rising shelf-edge trajectories, while the progradational ones are related to nearly horizontal shelf-edge trajectories. Rising shelf-edge trajectories indicate the rising of the Pannonian Lake level, while horizontal shelf-edge trajectories reveal steady state lake level.

To observe the typical morphological elements of aggradational and progradational period, spectral decomposition from shelf related horizons were performed. Applying spectral decomposition is useful to indentify the lateral geological discontinuities with higher certainty. To transform time domain to frequency domain

Discrete Fourier Transform (DFT) was applied within time gate of  $\pm 25$  ms around each selected horizon slice. Red-green-blue (RGB) maps were made by the blending different frequencies (Fig. 1.).

RGB colour blended map shows depositional environments of shelf to basin floor. With this method stratigraphic features, such as shelf-edge, slope canyons, toe-of-slope lobes and structural settings became obvious.

In some part of the study area the prograding delta on the shelf could be recognized, indicating that taking into account the seismic resolution, the height of these delta features are up to 40-50 m.

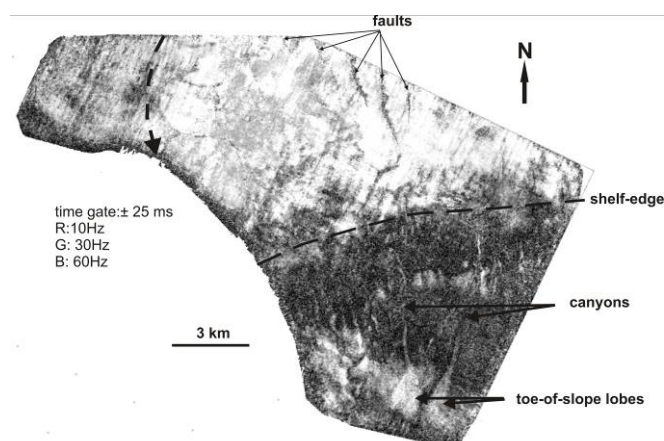


Fig.1. Spectral decomposition map and red-green-blue (RGB) colour blending of a seismic horizon shows depositional environments of shelf to basin floor.

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## Uranium and REE enrichment of the phosphatite occurrence at Pécsely (Balaton Highland, Hungary)

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The study area is located in the Balaton Highland, in the southwestern part of the Transdanubian Range, which is composed mostly of Triassic formations. Earlier investigations have revealed radioactive anomaly in the vicinity of Pécsely, which was caused by a uranium-bearing sedimentary phosphatite indication (Kiss & Virágh, 1958). Though according to this study, the host rock of the phosphatite is the Megyehegy Dolomite Formation, according to latest results, it is hosted by the Vászoly Limestone Formation (Budai *et al.*, 1999). This formation is unconformably overlying the Anisian Tagyon Limestone Formation (platform carbonate), and has formed as a basinal carbonate with volcanic tuff intercalations in the Upper Anisian (Budai & Haas, 1997; Budai & Vörös, 2006).

The studied uranium-bearing layer is located in Triassic limestone while epigenetic fluorite veins are found in the older, underlying dolomite. The phosphatite is thought to have formed syngenetically with the limestone, during its deposition. The horizontal extension is large, but the small thickness (0.5-3 cm) of the mineralized layers makes the indication – from the practical point of view – rather unpromising. The main mineral found in the layers is carbonate-fluorapatite, but calcite, rare hematite, pyrite and zircon also occur. The phosphatite layers are finely banded, and contain desiccation cracks on their surfaces (Kiss & Virágh, 1958). By far the genesis of this layer and the veins are not well documented, so this work aims to contribute to our knowledge on the characteristics and origin of the mineralization.

Based on the petrographical observations, the carbonate-fluorapatite is located around the grains of the rock-forming calcite whereas the remaining space is filled by a later generation of calcite cement. Sometimes rock-forming dolomite is brecciated and has a phosphatitic cement. Fluorite found below the phosphatite layers is euhedral (0.1-2 mm) and is of dark purple colour. The fluorite crystals form veins and fill small cavities with minor amounts of calcite. Fluorite can also be found finely dispersed in the matrix of the host rock in which brecciated clasts of the phosphatite layers can be also found. The cathode luminescence pictures of the fluorite shows a fine zonation (Fig. 1.), which may be caused by the radioactivity of the phosphatite layers.

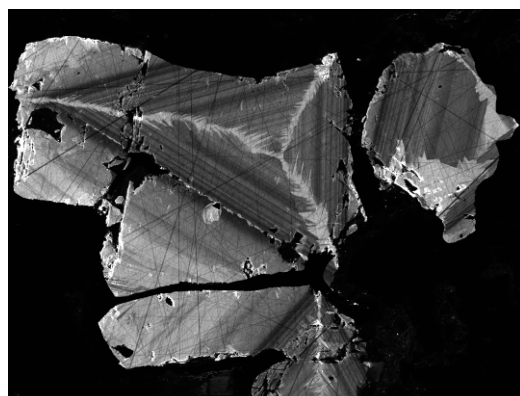


Fig. 1.: Cathode luminescence picture of the fluorite

Quantitative analyses (EPMA) of phosphatite grains showed, that they contain 5.9-7.855 mass% F, 41.621-53.759 mass% CaO, 25.169-36.993 mass% P<sub>2</sub>O<sub>5</sub> and 1.013-1.762 mass% SO<sub>3</sub>, which does not match exactly the theoretical composition of carbonate-fluorapatite. Furthermore 0.013-0.3 mass% UO<sub>2</sub> and 0.029-11.982 mass% FeO, 0.066-0.104 mass% TiO<sub>2</sub>, 0.043-0.104 mass% MgO, 0.024-4.625 mass% SiO<sub>2</sub>, 0.02-0.028 mass% MnO, 0.04-0.073 mass% La<sub>2</sub>O<sub>3</sub>, 0.036-0.059 mass% Ce<sub>2</sub>O<sub>3</sub>, 0.032-0.104 mass% Nb<sub>2</sub>O<sub>5</sub>, 0.099-0.124 mass% Dy<sub>2</sub>O<sub>3</sub>, 0.147 mass% Sm<sub>2</sub>O<sub>3</sub>, 0.032-0.038 mass% Nd<sub>2</sub>O<sub>3</sub>, 0.051-0.098 mass% Tb<sub>2</sub>O<sub>3</sub>, 0.027-0.075 mass% Pr<sub>2</sub>O<sub>3</sub>, 0.181-0.242 mass% Ta<sub>2</sub>O<sub>5</sub>, 0.031-0.51 mass% Y<sub>2</sub>O<sub>3</sub>, 0.016-0.177 mass% Gd<sub>2</sub>O<sub>3</sub> and 0.045-0.059 mass% Eu<sub>2</sub>O<sub>3</sub> occur. The data analysis revealed that, the uranium and sulphur content and the uranium and calcium content correlate positively, while uranium and phosphorus show negative correlation. The fluorite contains 48.155-52.178 mass% F, 38.132-49.135 mass% Ca and 0.009-0.038 mass% P and may contain a small amount of Al (0.01 mass%), Ti (0.038-0.054 mass%), Mg (<0.016 mass%), Mn (0.022 mass%), S (0.014-0.028 mass%), Si (0.012-0.021 mass%), Nb (0.022-0.03 mass%), Dy (0.08 mass%), Sm (0.154 mass%), Gd (0.027 mass%), Eu (0.094 mass%) and U (~0.01 mass%). Elemental mapping prepared of the fluorite revealed, that its REE content is most likely related to submicron sized REE mineral inclusions.

Uranium appears as a trace element in the phosphatite grains and in the fluorite, no uranium minerals were identified. The source of the U was probably an older rock, e.g. the Permian alluvial sandstone, which can be found nearby, and its U content is already proven (Budai *et al.*, 1999). The relatively high phosphorous content may derive from the large amount of fishbones and other organic particles of the rock (Kiss & Virágh, 1958), but the concentrating role of a (hydrothermal) fluid has to be taken into consideration, too (see the euhedral carbonate-fluorapatite crystals in the cavities of the phosphatite layers). As brecciated phosphatite clasts occur also in the fluorite bearing rock, it is suggested that the fluorite formed later, than the phosphatite. The dark purple colour of the fluorite can be the result of its radioactive material content. Consequently, the fluorite of this locality may have formed by the leaching of the fluorine content of the carbonate-fluorapatite and the rare earth elements can also be derived from the phosphatite layers.

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# Re-examination of the historical ore samples from the Au-Ag-Pb-Zn epithermal mineralisation around Parádfüzdő, Recsk Ore Complex (NE-Hungary)

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The Paleogene Recsk Ore Complex consists of a Cu-Mo(-Au) porphyry, Cu-Zn skarn and metasomatic Pb-Zn ore mineralisation at depth, while the shallow volcanic cover contains epithermal Cu-Au-Ag and Au-Ag-Pb-Zn mineralisation. The aims of our study are to re-examine the historical samples from the shallow Au-Ag-Pb-Zn ore mineralisation around Parádfüzdő, and to refine our knowledge about this mineralisation in order to understand the formation of the ore complex.

The studied mineralisation is located above the mineralised diorite intrusion and hosted by altered dacite and dacitic tuff units. The most widespread alteration of this area is the intermediate argillic alteration with sparse kaolinitization (Molnár, 2007; Molnár *et al.*, 2008). The ore mineralisation is controlled by siliceous veins (Hegyeshegy, Orczy and Antal Adit) and hydrothermal breccia dykes (Macskahegy, Etelka, Orczy, Egyezség, Józszomszéd and Veresagyagbérc Adits).

Reflected light and scanning electron microscopy with standardized energy dispersive X-ray analysis were used to identify the ore minerals and to observe the precipitation sequence of these minerals (Fig. 1.). Quartz crystals are always related to the ore minerals and usually precipitated at the early stages of the ore formation. The ore formation usually started with the precipitation of pyrite, but in some adits (Orczy, Etelka, Antal, Hegyeshegy and Macskahegy Adits) these pyrite crystals contain bornite, calaverite, hessite, wittichenite and aikinite grains. The presence of aikinite and wittichenite has not been known previously (Nagy, 1983, Kisvarsányi, 1954) in the area. Two different pyrite textures were observable in the samples; the euhedral pyrite crystals with mineral inclusions and the collomorphous pyrite with pseudomorphs after marcasite. The first one is present in every sample, while the collomorphous pyrite was only observable in the Veresagyagbérc

and Macskahegy Adits. Then galena and sphalerite precipitated in locally different quantities. The last formed minerals are the tetrahedrite and tennantite. The tetrahedrite is more dominant in the Józszomszéd, Orczy, Antal, Macskahegy and Veresagyagbérc Adits, while the Egyezség, Etelka, Macskahegy, Hegyeshegy Adits are characterized by tennantite. The fahlore is usually associated with chalcopryrite and in the Hegyeshegy Adit with achantite. The chalcopryrite usually represents a boundary between the sphalerite and fahlore crystals and forms small inclusions in sphalerite. According to the study of Bortnikov and *et al.* (1991) this chalcopryrite presumably formed as a reaction product, when the FeS content of the sphalerite reacted with the Cu-rich fluid, which formed the fahlore crystals at the final stage. This well-defined event can be traced in most of the adits.

Considering the above mentioned mineral phases more than one ore forming stage can be distinguished. The samples from the different adits beautifully represent these stages with their mineral composition.

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	Józszomszéd adit	Egyezség adit	Orczy adit	Etelka adit	Antal adit	Hegyeshegy	Macskahegy	Veresagyagbérc
quartz	—	—	—	—	—	—	—	—
pyrite	—	—	—	—	—	—	—	—
galena	—	—	—	—	—	—	—	—
sphalerite	—	—	—	—	—	—	—	—
tetrahedrite- tennantite	—	—	—	—	—	—	—	—
chalcopryrite	—	—	—	—	—	—	—	—
bornite	—	—	—	—	—	—	—	—
hessite	—	—	—	—	—	—	—	—
calaverite	—	—	—	—	—	—	—	—
wittichenite	—	—	—	—	—	—	—	—
aikinite	—	—	—	—	—	—	—	—
tetradymite	—	—	—	—	—	—	—	—
acanthite	—	—	—	—	—	—	—	—
covellite	—	—	—	—	—	—	—	—

Fig.1. Observed succession of the ore minerals in different adits (from North to South)

## **Application of 2D and 3D geoelectrical resistivity method for engineering site investigation**

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Orthogonal set of 2D geoelectrical resistivity field data in Zone 16 were studied. In this locality, the establishment of complex multi-floored buildings for residential and commercial purposes was planned. This locality was divided into seven sub-zones.

In each sub-zones, orthogonal profiles were collected by Schlumberger soundings array. ID layering information and supplement to the orthogonal 2D profiles were also provided. The observed 2D apparent resistivity data were first processed individually and then collated into 3D data set which was processed using a 3D inversion code. The 3D model resistivity images obtained from the inversion are presented as horizontal depth slices. Some distortions observed in the 2D images from the inversion of the 2D profiles are not observed in the 2D images extracted from

the 3D inversion. The survey was conducted with the aim of investigating the degree of weathering and fracturing or cavities in the area under investigation.

The weathered profile and thereby ascertaining the suitability of the site for engineering constructions is presented, as well as the determination of its groundwater potential.

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## Magnetic survey on Neolithic site Vinča

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An archaeological site of the Neolithic culture of Belo Brdo (White Hill) is situated on the right bank of the Danube River in the village of Vinča, 14 km downstream from Belgrade. It was first discovered in 1908 by the Serbian archaeologist Miloje Vasić (Vasić, 1932). Since then, with several interruptions, numerous archaeological excavations have been carried out.

The last campaign was finished a few years ago (1998–2009). Vinča-Belo Brdo was introduced into the treasury of world heritage as an object of prehistoric cultures. It is almost entirely made up of the remains of a human settlement and was occupied several times from the Early Neolithic (ca. 5000 BC) through to the medieval period (Nikolić & Vuković 2008; Srejšović & Tasić 1990). Serbian Government warranted it the highest level of state protection and classifies it as an archaeological site of exceptional importance. Today, Vinča has the status of Archaeological Park. Unfortunately the site has received no appropriate treatment in practice.

Protected area is much smaller than real area where people from that time have lived and have leaved artifacts. Archaeological remains are covered with present village and infrastructures (roads, houses, cables, pipes etc., see Fig. 1.). Use of magnetometer survey was test in this unfriendly environment for magnetic survey.



Fig. 1.: Location of research area (maps.google.com)

Detecting a concentration of burned objects (fireplaces, kilns, fired clay) by magnetic measurements is one of the best known archaeogeophysical applications (Breiner, 1973).

The magnetic measurements were made using an Overhauser GSM-19W proton magnetometer with an absolute accuracy of  $\pm 0.1$  (nT), resolution of 0.01 (nT) and sampling interval of 0.5 (s). We use gradient walk mode, for collecting data, without GPS (Global Position System). We measured data on two fields. Spacing between profile lines was 0.5 m, where it was possible. Azimuth of profiles was 60 degrees. Sensors was at heights of 0.9 m and 1.74 m above ground. Geodesy provides us positions of the field edges. After data correction, vertical gradients were computed (Fig. 2.) to one field. Kriging interpolation method was used for vertical gradient map. In down right corner we had to remove bad data caused by an iron fence. Data were removed manually. Field can be separated to north and south field by difference in height field.

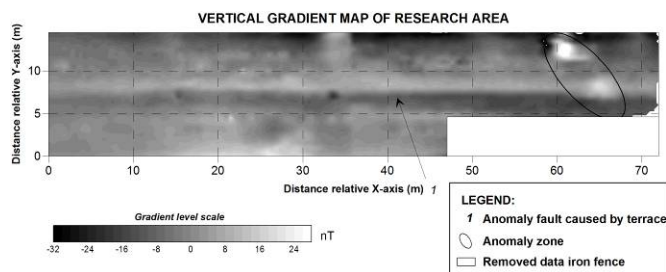


Fig. 2.: Vertical gradient map of magnetic survey

North part of the field is 0.1 to 0.3 m higher from south part. Magnetic survey shows, that it is like dipole line with maximum on north and minimum on south side of line. The magnitude of dipole does not affect the results of the research.

Aim of research was to detect possible remains of fireplaces and houses. Positive magnetic anomalies of gradient over 20 (nT) could be buried remains.

In the coming period, we will try to estimate the depths of the anomalies. Presented data shows that magnetic survey can be used in some cases inside populated areas with infrastructures, too.

Regarding archaeological tasks, results from our surveys benefited the archaeology team to better choose the locations for archaeological sounding.

After sounding we will have clear image of the site. We will be able to measure magnetic susceptibility. We will use it as an input parameter for depth calculation and prediction of the interesting anomaly fields.

All previous results give us better starting position for the next explorations of wider zone of archaeological site Vinča.

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## Mineralogical investigation of soils formed on carbonate rocks in the Bükk-Highlands (Hungary)

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The primary aim of our mineralogical investigation was to study the mineral composition and the soil-forming materials of the soils in the native forests of the Bükk Mts. The investigated soils can be found at the top of the Bükk Mts., on the so-called Bükk Highlands. This limestone plateau is composed primarily of limestone but contains also dolomite and shale. In the course of our investigations we have analysed four soil profiles. The formation of the acidic and humus rich upper layer of the soil profiles is influenced by the mineral composition and the weathering of the rocks. In order to study the composition of soil minerals thermoanalytical and X-ray diffraction measurements have been carried out. Different soil particle fractions have been analysed by polarizing microscopy. According to the thermal analyses the most abundant mineral in the soil samples was quartz, accompanied by clay minerals and oxides-hydroxides (Földvári, 2011, Zagórski, 2010) (Fig. 1). The presence of calcite could only be evidenced in a few samples. The X-ray diffraction measurements have also confirmed these findings, because according to this we can say that quartz represents the most significant proportion in all of the soil profiles, and besides quartz, clay minerals, feldspar and oxides-hydroxides also occur; respecting calcite we have got interesting results, as this mineral appears only in four layers and in very little concentrations in all of the soil profiles (Fig. 2.).

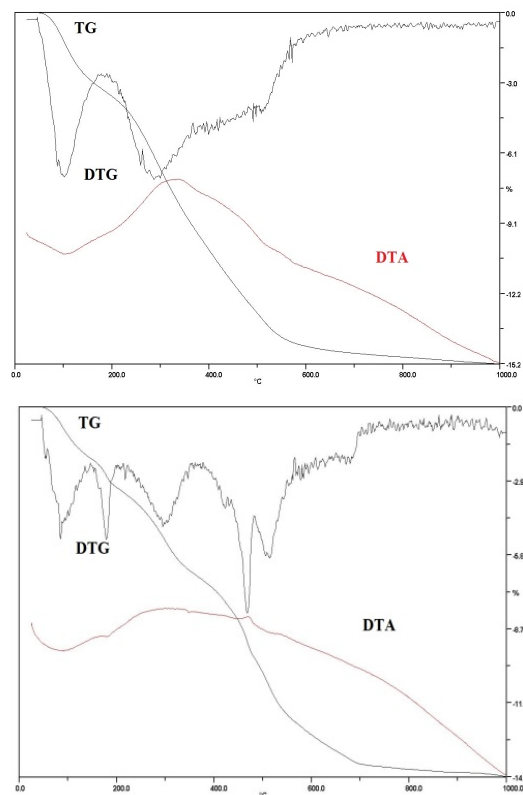


Fig. 1.: Thermal analysis results of some of the soil samples.

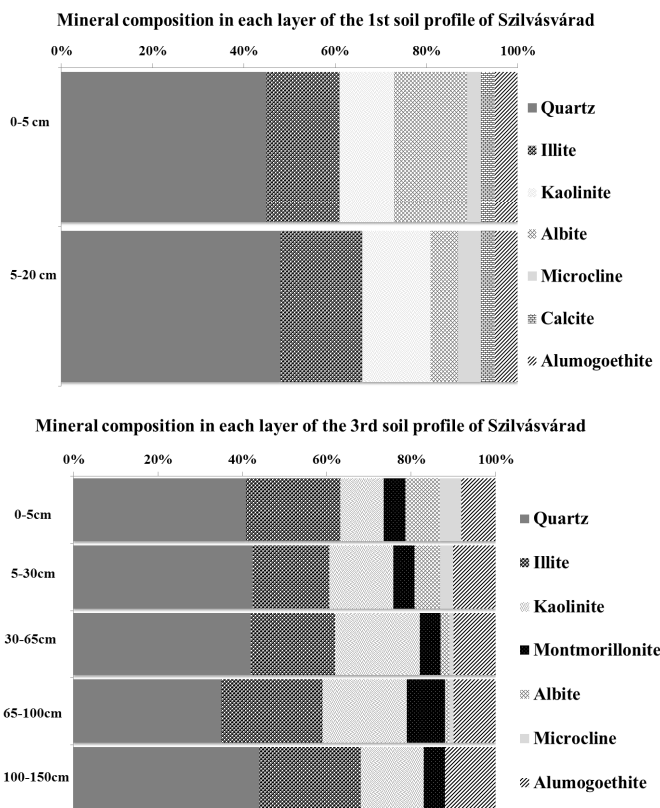


Fig. 2.: X-ray diffraction results of some of the soil samples.

X-ray analyses have also revealed the presence of alumogethite in each of the profiles, a mineral, indicating a previously warmer and humider subtropical climate. This warmer climate of the area has been periodically changing for over 65 million years with a colder and dryer climate and these changes also affect the development of the soils.

The investigated soil samples of the Bükk Highland contain significant amounts of silicates, so apparently they cannot be the product of the weathering of limestone solely. The major part of soil-forming material originates presumably from previous dust fallings or the agglomerate materials of erosion.

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## Autonomous local water supply systems for remote settlements - Municipality of Ruma (Serbia)

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There are currently 51 registered public waterworks companies, which provide population of Serbia with water for domestic use. For years, there was a problem of water supply for smaller, remote settlements because there was no possibility of centralized water supply from one source. That problem is particularly evident in Vojvodina, because of the great distances among the settlements. In this paper, the development of several local water supply systems for smaller settlements in municipality of Ruma is presented.

Municipality of Ruma is located in Vojvodina, in Srem region. It occupies an area of 582 square kilometres. It is located between Fruška Gora Mountain on north and Sava River on south. There are 17 settlements in this municipality, from which, 16 has rural character and one is the city of Ruma. The entire population is estimated at 60 000, from which, about 50% lives in rural settlements.

There are two big water supply systems in the studied area and they supply the population of Ruma and surrounding settlements with water, while other settlements use local water supply systems for their needs. Some of these local supply systems are under jurisdiction of public communal company, while others are managed by local community.

necessary infrastructure (tanks and piping). Treatment is done in situ with chlorine insertion through the chlorinator.

Research consisted of several operations: observation of fluctuations of groundwater levels and yields over time as well as the determination of the chemical composition in order to determine the reserves of groundwater and to establish the water protection zones.

Geology: Researched formations are of Quaternary and Holocene age. Beneath of this sediments are the older formations starting from the Neogene sediments and on. Through the geological history, with deposition of sediments of Panonian Sea, water also stayed trapped. This water was, up to date, under the influence of a number of geological processes in time and space, and went through various changes. That is the reason why we today have different types of water at different depths.

Aquifer: All well screens are located in layers of sand and gravel, one layer at 55-75 m and other at about 80-90 m depth.

Regime: Biggest week average yield was 9.3 l/s and was measured in Mali Radinci, while smallest yield was in Nikinci and averaged 3.4 l/s. The biggest fluctuations in groundwater level were observed at Mali Radinci (16.53 m) while smallest were at Grabovci (4.38 m).

Chemistry: Groundwater from the local water supply systems is low-mineralized, with  $\text{HCO}_3\text{-Na}$  and  $\text{HCO}_3\text{-Mg}$  composition

The main problem of the examined water quality is the content of ammonia, iron and manganese ( $\text{NH}_3$ , Fe and Mn) with the exception of water in Dobrinč which meet all the requirements for drinking water quality.

Taking into account that the iron and manganese in the water appear under anaerobic conditions, their elevated concentration in groundwater from artesian horizons were expected. Ammonia in groundwater occurs mainly as a product of decomposition of organic matter. Together with the elements of nitrogen triad is an indicator of organic pollution of groundwater. But, ammonia may have an inorganic origin because this compound frequently occurs in the deeper parts of artesian and sub-artesian horizons. Given the absence of coliform bacteria and low consumption of  $\text{KMnO}_4$ , with low concentrations of nitrate and nitrite, it can be concluded that ammonia in these waters occurs as their natural ingredient and is not the result of pollution.

To summarize, when there are a large number of settlements within a municipality, centralized water supply system is not the best solution. Main pipelines are major investments, and there is always the risk of breakdowns and accidents which could lead to interruptions of water supply. Also, bigger demand for water could lead to overexploitation and well aging in main water supply systems. When the groundwater resource is not an issue, like in the case of municipality of Ruma, the optimal solution is that all the remote settlements have autonomous water supply system.

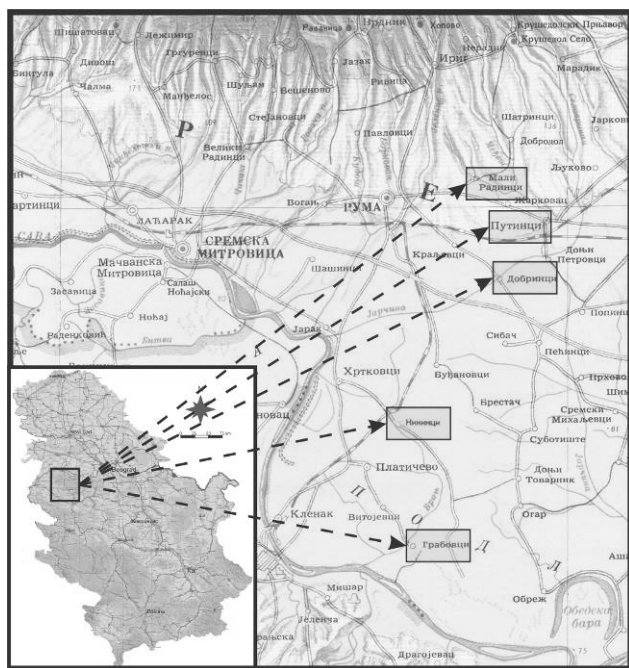


Fig. 1.: Map with locations of research areas

In this paper, the development of five local water supply systems is presented. (Fig. 1.). Settlements Dobrinč, Grabovci and Nikinci use water from local wells for supply, while Mali Radinci and Putinci are parts of a regional system, but still have own wells for supply in case of a need. Groundwater exploitation is performed using vertical wells. All local water supply systems are equipped with the

## Fluid conditions of the formation of the veinlet-impregnated mineralization in the Zabolottia suite of the trap formation of the West Volyn (Ukraine)

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An analysis of fluid inclusions research in deposits of trap formation of the Lower Wendian of the West Volyn (Ukraine) (Naumko *et al.*, 2012) testifies that investigations of veinlet-impregnated mineralization as a direct indicator of migratory processes and products of healing of migration fractures (Svoren & Naumko, 2005), makes it possible to determine physical-chemical nature, spatial-temporal sequence of the manifestation and the changeability of indicators of parametric characteristics of fluids at post-magmatic phase and to reconstruct fluid conditions of mineral genesis in raw material deposits (Naumko, 2006).

We have used this approach for determination of temperature conditions and the composition of mineralizing fluids based on data of the studies of the mineral composition and investigations of fluid inclusions in analcimes and calcites from the veinlet-impregnated formations of the Zabolottia suite of the trap formation of the West Volyn.

The Zabolottia suite makes the beginning of the formation of the common section of the trap formations. The difference of the given basaltic formations is not important, from the point of view of the native copper mineralizations.

Nevertheless, investigation of this suite allows us not only to understand the reason of the absence of the mineralization in these rocks, but to explain the presence of native copper mineralization in other suites of the trap formation, to construct a genetic model of native copper mineralization, to proceed uniquely to the contouring of potentially ore-bearing fields and concrete prospecting areas.

According to X-ray analysis (analyst Ya. V. Yaremchuk), the veinlet-impregnated mineralization of the Zabolottia suite is represented by zeolites (analcime, chabasite, stilbite), that are concentrated mainly in amygdaloids, by quartz and calcite. In particular, in the section of the borehole 8265 from the basement to the cover one can observe the following picture: at a depth of 293.0 m (sam. 8265/206) it was found quartz, chabasite, calcite, stilbite; at a depth of 284.0 m (sam. 8265/166) – analcime, quartz, calcite; at a depth of 269.0 m (sam. 8265/8) and 255.0 m (sam. 8265/1) – analcime.

According to data of thermometric analysis it was possible to reveal conditionally-primary and secondary inclusions. By phase composition these are two-phase gas-liquid and liquid-gaseous, with significant predominance of gas-liquid inclusions. The highest temperature of homogenization of fluid inclusions fixed in analcime is 280°C (by conditionally-primary inclusions). The majority of inclusions are homogenized at the temperature intervals of 190–200±5°C and several inclusions were homogenized at temperature of 215–230°C. Very often one can observe phenomena of unlacing and refilling of inclusions, however, because of the fear of cracking during the lab test, repeated thermometric analyses were performed. Analcime is more earlier formation of veinlet-impregnated mineralization in comparison to calcite.

In calcite, gas-liquid inclusions are predominant and their size ranges from 0.1–0.01 mm. In most cases one can observe inclusions of a regular shape, which are concentrated in minerals as individual groups. These are mainly long quadrangles and negative crystals with well-developed faceted surfaces-primary fluid inclusions homogenization of which occurs at temperature of 70±5°C into liquid phase. Secondary gas-liquid inclusions are found as families in the healed fractures, the temperature of homogenization of which is 70±5°C into liquid phase. The presence of sufficient quantity of primary fluid inclusions testifies to calm conditions of the calcite forming.

The composition of volatile of fluid inclusions in minerals and close pores according to data of mass-spectrometry analysis, the relationship between nitrogen and carbon dioxide is defined (analyst B.Ye. Sakhno). Similarly to results obtained earlier for basalts of the Luchychi stratum (Naumko *et al.*, 2013), in most samples of the Zabolottia suite, nitrogen is considerably prevailing, too. Nitrogen content ranges from 36.6 to 90.7 vol. %, and for zeolites from veinlet-impregnated mineralization for the given suite – within the limits of 92.4–96.7 vol. %. Sometimes gas saturation is within the bounds of threshold sensitivity of the instrument.

In paper (Govtulja *et al.*, 1980) it is indicated on the increased content of N<sub>2</sub> composition of volatile in rhombic and monoclinic pyroxene as well as in plagioclase from andesite of the volcanic area of Sheveluch. Because plagioclase and pyroxene are minerals of early-magmatic origin, it can be supposed that during mineral formation a high-temperature early-magmatic fluid was acting. Nitrogen content (up to 100 vol.%) in zeolites may be explained by the special features of the structure which can be imagined as a kind of caverns of molecular size where nitrogen penetrates.

Therefore, fluidal environment of the mineral crystallization was in the state of two-phase equilibrium caused by heterogeneity of the mineral-forming fluid. Inclusions of heterogeneous origin testify to that. The availability of the families of uneven filling and manifestation of phenomena of unlacing and refilling of inclusions also indicate instability of the minerogenetic environment. Small depths of occurrence of the rock complexes contributed to this.

It is evident that forming and development of ore-generating system as the part of melt physicochemical system needs near-intrusive conditions. This suite do not reaches such conditions because of small thickness of flood and substantive gas saturation. This is the reason of low copper content in Zabolottia suite.

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## Gamma dose rate and radionuclides content in beach sands of Western Pomerania, Poland

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Natural background gamma radiation depends on high-energy cosmic radiation and terrestrial radionuclides content in the earth's crust. Main terrestrial radionuclides which are gamma-emitters responsible for external exposure to human beings are radionuclides of the  $^{238}\text{U}$  and  $^{232}\text{Th}$  decay series as well as  $^{40}\text{K}$ . The worldwide average outdoor absorbed dose rate that arise from the presence of these radionuclides in the environment is equal to  $58 \text{ nGy}\cdot\text{h}^{-1}$  (UNSCEAR, 2000).

Terrestrial radiation reflects geological background. In general, the igneous rocks (especially rich in alkali and silica) are more radioactive than the sedimentary rocks. Nevertheless, there are some exceptions, such as shales or phosphate rocks which may contain relatively high concentrations of radionuclides (UNSCEAR, 2000). Sands usually are characterised by low radioactivity, but some beach sands may contain elevated concentrations of U and Th. A few coastal regions of high background gamma radiation, e.g. in Brazil, India or Egypt are well investigated. Radioactivity of beach sands results from the presence of heavy minerals, such as monazite and zircon, which are carriers of U and Th (Abd El Wahab & Nahas, 2013). Contribution of monazite in heavy-mineral sand deposits may reach 4% (Tamil Nadu, India) and contribution of zircon 8% (Kerala, India) (IAEA, 2011).

Heavy minerals, as high-density material, tend to concentrate in areas of beach erosion; meanwhile minerals of lower density are deposited in areas of beach accretion. Heavy-mineral accumulations form dark strips parallel to the shoreline and situated in foreshore or backshore. Heavy minerals may also be concentrated behind obstacles (Vassas *et al.*, 2006).

The aim of the research was to investigate background gamma radiation and radionuclides concentration in beach sands in Międzyzdroje, Dziwnów and Rewal (western coast of Poland), especially in zones enriched with heavy minerals.

Measurements of uranium  $^{238}\text{U}$  (in ppm), thorium  $^{232}\text{Th}$  (in ppm) and potassium  $^{40}\text{K}$  (in %) content in beach sands have been conducted in situ by means of the portable gamma spectrometer RS230 with a BGO detector. A single measurement lasted 180 s. Measurements have been performed directly on the sands and 1 metre above the ground level. Two profiles, in Międzyzdroje and Dziwnów, with measurements at approximately 2 meters between shoreline and dunes have been arranged. In Rewal measurements have been performed directly on heavy-mineral sands concentrated behind obstacles.

Absorbed dose rate in  $\text{nGy}\cdot\text{h}^{-1}$  was calculated using the formula:

$$D = 0.043 \cdot S_K + 0.43 \cdot S_{Ra} + 0.66 \cdot S_{Th}$$

where  $S_K$ ,  $S_{Ra}$  and  $S_{Th}$  are activity concentrations of K, U and Th in  $\text{Bq}\cdot\text{kg}^{-1}$ .

Additionally, mineralogical analyses of beach sands from Międzyzdroje have been performed at the University of Silesia in Katowice by means of X-ray diffraction (XRD) technique.

One, 2-metre width, strip of heavy-mineral sands was observed in Dziwnów at a distance of approx. 8 m from the shoreline. Two

strips were observed in Międzyzdroje. The first one, 3-metre width, was situated approx. 10 m from the shoreline and the second one, 1-metre width, was located approx. 35 m from the shoreline, close to the dunes. In Rewal, accumulations of heavy minerals were observed behind a breakwater and behind an unused fishing boat.

Average absorbed dose rate in Międzyzdroje and Dziwnów at the level of 0 m was equal to  $42.8$  and  $28.4 \text{ nGy}\cdot\text{h}^{-1}$ , respectively and at the level of 1 m  $33.0$  and  $24.5 \text{ nGy}\cdot\text{h}^{-1}$ , respectively. The greatest values of absorbed dose rate were observed in zones of heavy minerals accumulation (Fig. 1.).

Average concentrations of K, U, Th in beach sands at the level of 0 m in Międzyzdroje were  $151.6$ ,  $30.1$ ,  $35.4 \text{ Bq}\cdot\text{kg}^{-1}$ , respectively and in Dziwnów  $178.0$ ,  $37.7$ ,  $6.9 \text{ Bq}\cdot\text{kg}^{-1}$ , respectively. Average concentrations of K, U, Th in heavy-mineral sands at the level of 0 m in Międzyzdroje were  $117.4$ ,  $70.7$ ,  $114.1 \text{ Bq}\cdot\text{kg}^{-1}$ , respectively and in Dziwnów  $151.3$ ,  $52.9$ ,  $8.4 \text{ Bq}\cdot\text{kg}^{-1}$ , respectively.

XRD analysis of PW sample from Międzyzdroje showed the presence of zircon (4.3%). Concentrated PW sample contains 4.6% of zircon and 0.5% of monazite; meanwhile concentrated PB sample contains 8.4% of zircon.

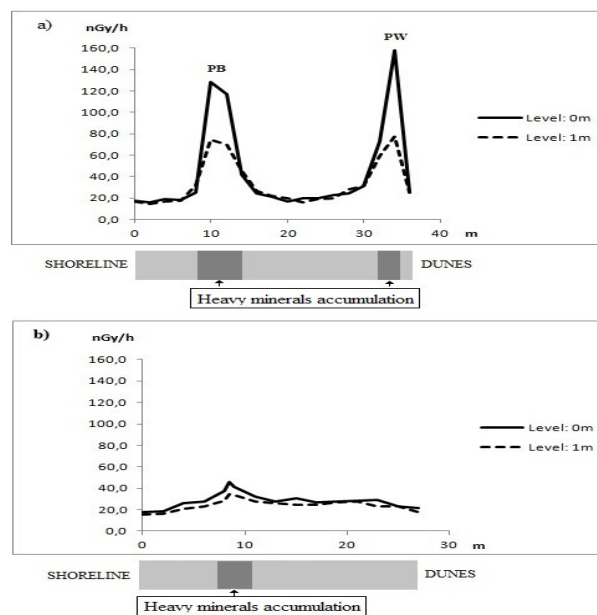


Fig. 1. Absorbed dose rate ( $\text{nGy}\cdot\text{h}^{-1}$ ) between shoreline and dunes along the profile in Międzyzdroje (a) and Dziwnów (b)

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## Fenitization processes in Chernigovka (Ukrainian Shield), Dubravinka (Voronezh Massif) and Penchenga (Yenisey Range) linear carbonatite massifs: similarities and differences

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Linear carbonatite massifs are potential sources of phosphate raw material, LREE and a wide range of rare metals (Nb, Ta, Sr, etc.). The typical feature of these formations is the occurrence of thick fenite haloes, which are forming over different compositional primary rocks. Whereas fenite halo dimensions are much more, than carbonatite bodies, usage of mineral association changes data and features of major and trace elements behavior during fenitization can contribute to prospecting work. The aim of the current research is to reveal and study such behavior regularities at the example of three linear carbonatite massifs: Chernigovka (Ukrainian Shield), Penchenga (Yenisei Range) and Dubravinka (Voronezh Massif).

All mentioned massifs are representatives of the linear structural-morphological type (Glevasskii *et al.*, 1981; Shnyukov 1988; Vrublevskii *et al.*, 2003; Dunaev, 2006). They are situated within a consolidated portion of the earth's crust, confined to deep-seated fault zones and occur as different morphology steeply-dipping bodies. Chernigovka and Penchenga have a linear form in a plan view, at the same time Dubravinka is crescent-shaped, which is considered as a similarity with classic carbonatite ring-complexes by some scientists (Dunaev, 2006). Thick exocontact fenite haloes are developed over different primary rocks, which are represented by migmatized Achaean metamorphic rocks in Chernigovka (amphibolite, gneiss, schist) and Dubravinka (gneiss) Massifs and Proterozoic metamorphic silicate (schist and amphibolite) and carbonate (marble) rocks in Penchenga Massif. So the most significant difference is the presence of marbles in Penchenga one, which considerably influences the character of fenitization products. The ore mineralization is partially different; apatite-rare metal in Chernigovka and Penchenga in contrast to apatite-magnetite in Dubravinka.

The formation age of the massifs of Chernigovka and Dubravinka are close – ~2.0 Ga (Glevasskii *et al.*, 1981) and 1.99–2.19 Ga (Dunaev, 2006), respectively. Penchenga massif rocks have been formed later – 0.672±0.093 Ga ago (Vrublevskii *et al.*, 2003).

Carbonatites mineral composition of the three studied massifs is similar: calcite-dolomitic, essentially dolomitic or calcitic; silicate minerals are micas, amphiboles and alkaline pyroxenes; all three massifs are apatite-enriched (its content varies from 5 to 25%, sometimes reaching 50%). Accessory and ore minerals are represented by magnetite, pyrochlore-gatchettolite, ilmenite, monazite, zircon, titanite, columbite, fersmite, sulphides (Glevasskii *et al.*, 1981; Dunaev, 2006; Vrublevskii *et al.*, 2003). However, a number of differences occur in each massif. Dubravinka Massif carbonatites are mainly calcitic and sufficiently melanocratic (silicate minerals content up to 50%), there is no pyrochlore-gatchettolite in them and garnet (schorlomite) occurs. Penchenga Massif carbonatites are calcite-dolomitic or essentially dolomitic, as Chernigovka Massif varieties, but in contrast to the last one, they are not containing alkaline pyroxene and olivine.

Fenitization in all massifs is also similar and is characterized by the disappearance of relict minerals (quartz, plagioclase, hornblende, micas, clinopyroxene) and the emerging of newly

formed minerals (albite, microcline, amphiboles and alkaline pyroxenes, biotite, phlogopite, calcite) and considerable rising of apatite content (up to ore concentration). Accessory minerals assemblage are represented by apatite, pyrrhotite, pyrochlore, titanite, titanomagnetite, ilmenite, (Penchenga); titanite, apatite, allanite, magnetite (Chernigovka); and apatite, magnetite, titanite, garnet (Dubravinka). But each massif are characterized by certain specific features; the absence of alkaline pyroxene in Penchenga Massif; different amphiboles (Penchenga – arfvedsonite, richterite; Chernigovka – richterite, edenite, hastingsite; Dubravinka – arfvedsonite); and the absence of pyrochlore-gatchettolite and presence of schorlomite in Dubravinka Massif. In general, the main direction of the different host rocks changes during fenitization is a convergence of their mineral compositions.

Studying the major and trace element behavior during the fenitization of the host rocks allowed revealing different groups of elements for each massif: elements, which are gained, elements, which are lost, and elements, which are redistributed. Using such differentiation, the single multiplicative zonation index has been suggested:

$$K_{univ} = La \cdot Ce \cdot Sr \cdot Zn$$

It is composed of elements, which are characterized by stable gaining and are not responsible for rocks ore burden. This makes it possible to observe changing of main ore components during fenitization (Fig. 1.). Thereby, this universal for all three massifs index objectively displays the increasing of host rocks transformation level and can contribute to the process of area selection and target evaluation.

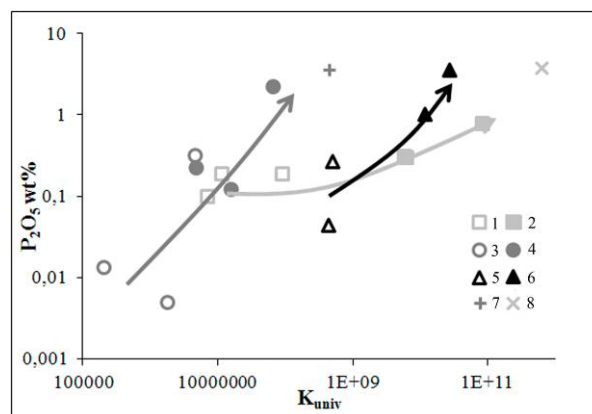


Fig. 1.:  $P_2O_5$  concentration changes (average composition) during primary rocks fenitization. 1-2 – Chernigovka massif rocks; 3-4 – Dubravinka massif rocks; 5-6 – Penchenga massif rocks (1, 3, 5 – unaltered; 2, 4, 6 – altered); 7-8 – carbonatites of Dubravinka and Chernigovka, respectively. Arrows – the direction of host rocks composition changes.

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**Micromineralogy for raw material determination of ancient ceramics – Case study on Roman amphorae, Istria, Croatia**

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Amphora is a special type of vessel that was used in the wholesale trade for transporting food (e.g. olive oil or wine) in the Roman Empire. The study of amphorae provides an insight into trade routes and ancient manufacturing technology. One of the best documented amphora workshops was located in Fažana (south Istria, Croatia). The workshop was owned for a long time by the Roman Laecanius family. The olive oil produced between 45-40 B.C. and 78 A.D. was shipped in amphorae to northern Italy and the provinces beyond the Alps. In the golden age of the workshop 10-12,000 Dressel 6B type amphorae were manufactured annually. The nearly 0.90 m high amphorae had scarcely 1cm thin wall. During the long-distance land and water transportation they were full of valuable products, so they had to be perfectly shock resistant and pressure-tight but also cheap enough because of their disposable use. The amphorae required high quality raw material, but the exact composition and origin of the raw material used in Fažana is still unclear.

Dr. 6B type amphorae of investigated time period were analysed by both archaeological and geological methods. Thin section petrography and fabric analysis show the raw material and the manufacturing technology. XRD can specify the plastic components and the firing temperature. Micromineralogy and heavy mineral analysis provide information about the nonplastic components of the paste and temper of the amphorae.

According to former thin section petrography and comparative heavy mineral analysis, terra rossa (the red soil of the Mediterranean, common in south Istria) was thought to be the only major source of the paste of Laecanius amphorae. Later new style petrographic studies suggested that the paste was a mixture of terra rossa and flysch (limestone, sandstone, siltstone and claystone bearing rock assemblage, common in north Istria), but their exact place of exploitation and proportion of use for the final paste is still unknown.

In this work the heavy mineral analysis occurred with a new, reverse approach, which starts with precise mapping of the heavy

minerals of possible raw materials. For heavy mineral analysis terra rossa and flysch samples were collected from the Istrian Peninsula. After dissolution in HCl and wet sieving, heavy minerals were separated (two fractions: 63-125 µm and 125-250 µm) in bromoform. From the obtained heavy minerals we made 26 different preparations. Stereomicroscopy, polarizing microscopy and scanning electron microscopy were used in quantitative and qualitative analysis of heavy minerals.

On the base of recent heavy mineral study of terra rossa and flysch samples, significant differences could be established. The coarse grained fraction consists mainly of authigenetic opaque mineral grains in both formations. The fine fraction is more varied: terra rossa samples consist mainly of minerals of the epidote-group, garnets and blue-green amphiboles, while in the flysch rocks epidote and amphibole are absent, however Cr-spinel is significant. Both terra rossa and the flysch rocks contain zircon, rutile, tourmaline and staurolite in small quantities, but their shapes and colours are basically different. Several flysch samples also contain foraminifers filled with opaque minerals (mainly pyrite) and elongated ferrous particles. Minerals in terra rossa samples are typically idiomorphic- hypidiomorphic, while in flysch samples are hypidiomorphic-xenomorphic.

In our study we have gained important qualitative and quantitative information on the heavy mineral composition of the Istrian terra rossa and flysch - as the two presumptive raw materials for Istrian amphorae. Thus by the heavy mineral analysis of Laecanian amphorae we will have better chance to determine more precisely, what kind of raw materials were used and in what proportion were they mixed for the paste of the amphorae in the Fažana workshop. Moreover, our results should help in raw material research of other amphora-producing workshops in Istria. Application of presented new style heavy mineral study can help to get more reliable knowledge about preparation of paste for different fired pottery products in wider range of space and time.

## Genesis of the exhalative iron ore occurrence of the Darnó Hill (NE Hungary)

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The Darnó Unit (in northeastern Hungary) is the uppermost nappe of the Bükk Unit, which has a rather complex geological structure in the Pannonian Basin. It fundamentally consists of Paleozoic, Triassic and Jurassic igneous and sedimentary blocks, related to different evolutionary stages (i.e. advanced rifting and back-arc-basin opening) of the Neotethys, which are found in an accretionary mélange complex (Kiss *et al.*, 2010 and references therein). The studied iron ore occurrence is found in one of the Triassic sedimentary blocks of this unit. It was described and last time intensively studied by Kiss (1958). By that time, there were many unclear questions about the geology of the area, which resulted in the uncertainty about the genesis of the mineralization. In the last decade, intensive research resulted in the above mentioned widely accepted model for the geology of the Darnó Hill area (Kovács *et al.*, 2010 and references therein). That is why the re-examination of the indication can provide important new information and also answer some unclear questions.

The studied samples were collected at the northern part of the Darnó Hill, and they are mainly composed of quartz and hematite. In the studied locality, hematite containing siliceous sedimentary rocks and coarser grained quartz and hematite containing rocks of most likely hydrothermal origin were also found. The former type is assumed to be the host rock of the mineralization. In the latter type, the hematite may form crystals up to 100 µm in size, and appears sometimes as thin plates, the habit of which suggests crystallization from warm hydrothermal solutions. However, at some places, the hematite can be found as fine-grained crystals, too, which may refer to lower formation temperatures. The syngenetic quartz is mainly massive, but in small cavities (0.5-1cm) sometimes idiomorphic crystals of 0.5 mm in length also occur. Polarization microscopic study revealed the presence of prehnite, while the EPMA study proved the occurrence of minor amounts of manganese-oxide, barite and apatite, together with the above mentioned minerals. The EPMA analyses have shown, that the hematite is rather rich in trace elements; it contains 3.5-4.5 w% Al<sub>2</sub>O<sub>3</sub>, ~0.1 w% TiO<sub>2</sub>, V<sub>2</sub>O<sub>5</sub>, MgO, 0.05 w% MnO and 0.01 w% ZnO, too. Based on the textural features, the paragenetic order can

be established, so first the hematite crystallised, followed by the prehnite, while quartz was continuously present in the system.

Bulk chemical analyses have shown some characteristic features, e.g. Fe>>Mn, or the typically low Ni-Co-Cu-Cr content. These characteristics are typical, when iron ore is the result of not exclusively sedimentary processes (Bonatti *et al.*, 1972; Bonström *et al.*, 1979), thus supports the submarine hydrothermal origin.

The quartz, which is cogenetic with the supposedly hydrothermal hematite, contains rarely small primary (5-10µm), two-phased (liquid and vapour) fluid inclusions with 5 to 10% vapour content. The minimum formation temperatures (i.e. the homogenisation temperatures) show a wide dispersion (70 to 155°C), which can be explained by the rapid cooling of the hydrothermal system. Furthermore the measured salinities (~4 NaCl equiv. wt%) suggest that the fluid was slightly enriched in salts as compared to sea water.

Based on these data, a sedimentary exhalative (SEDEX) origin is supposed for the studied indication. It can be classified to the magmatic origin type, volcanics- to sediment-hosted iron deposit subtype according to the taxonomy of Dill (2010). However, it fits well to the geological model of the Darnó Unit, as SEDEX deposits may typically form in the (advanced) rifting stage.

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## Synthesis and structural examinations on LTA-type zeolite

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Zeolites were just curiosity for a long time, but nowadays the usage of their name is increasing and zeolites become very important materials in environmental issues and industry. For what thanks this approach changes? As usual, the main progress in the knowledge on zeolites was the successful structure determination.

Zeolites have a complex aluminosilicate frameworks structures. These frameworks are opened with large channels and interconnected cages. We can use zeolites in gas and petroleum industry, water softening, sewage treatment, agriculture, paper production, radioactive waste treatment as well as construction materials too. The structural channels and voids are occupied loosely bound cations and water molecules that we can remove and replace without disrupting the tetrahedral framework. This means that a zeolite structure is among the best candidates to perform cation exchange, adsorption molecular sieving (passing a gas or liquid through a zeolite), dehydration and rehydration processes, in addition it can be resistant to high energy radiation, too (Tschernich, 1992).

The present work focuses on preparation and structure determination of sodalite-related zeolites using X-ray and electron diffraction techniques. I synthesized LTA-type zeolite crystals from metakaolinite starting material with alkaline (NaOH) method. Then I replaced  $\text{Na}^+$  with  $\text{Cs}^+$ , and measured the resulted structural changes, using X-ray powder diffraction.

The LTA crystals revealed cube and sphere shapes under scanning electron microscope (Fig. 1.).

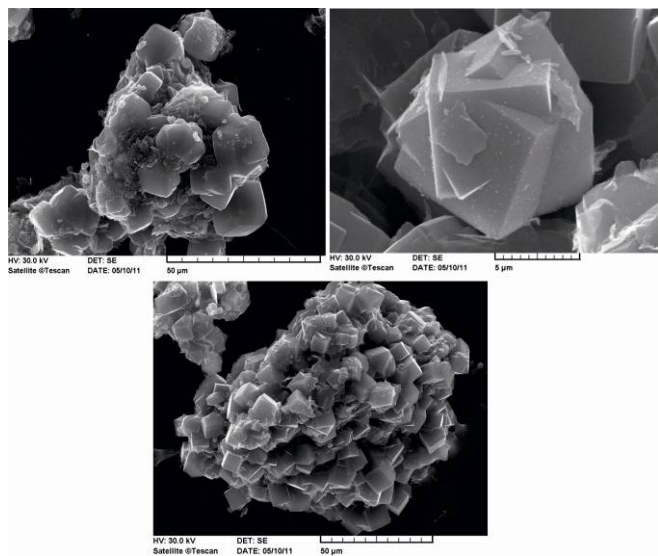


Fig. 1.: It was treated for 24 h with 3 mol NaOH. LTA-s hexahedron and rhombohedron, these have 8 to 11  $\mu\text{m}$  edge length. We observed spheres with 1  $\mu\text{m}$  size.

X-ray powder diffraction measurements on Na-LTA, acid treated LTA and Cs-LTA were performed. The hkl and intensity data sets were the inputs of structure determination using the SIR (Semi Invariant Reconstruction) and SHELX program packages. Due to overlapping reflections, some sample resulted in high R factor values. However, the resulted LTA-type framework proved to be evident (Fig. 2.).

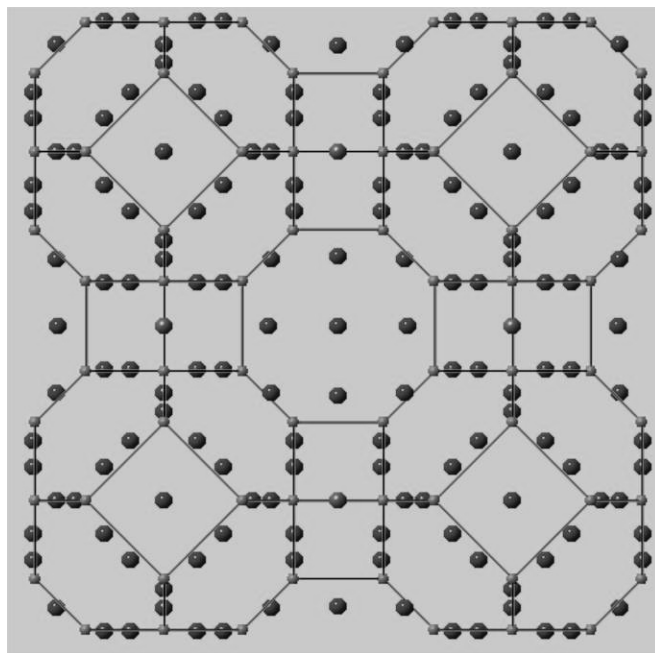


Fig. 2.: Na-LTA zeolite structure determined by SIR

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## Distal tephra layers of the Ciomadul volcano

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In the present study I show the results of the volcanological examination, including physical volcanology, petrography and geochemistry of the tephra layers from the Ciucului and Braşovului Basins located in the SE edge of the Carpathian-Pannonian Region. Three localities were studied in details called here as locality 1 (Northeast from Târgu Secuiesc) and locality 2 (East from Turia) in the Braşovului (Háromszéki) Basin; locality 3 (Northeast from Sânmartin) in the Ciucului (Csíki) Basin.

Locality 1 (lc1) hosts a pumiceous lapilli layer embedded in quaternary sediments of the Turia brook terrace. The medium-well sorted tephra layer has a constant (~25 cm) thickness, suggesting that this layer is related to the tephra fallout, as suggested by Vinkler *et al.* (2007). Locality 2 (lc2) can be found only 9 km far from lc1. It hosts a pumiceous layer that probably represents the same layer as found in lc1. This layer is ~10 cm thick and consists of medium-well sorted lapilli. Below this, a series of coarse and fine grained ash layers was found. The pumice and ash layer series is separated by siliciclastic sediments. Locality 3 (lc3) hosts a ~35 cm thick coarse grained ash layer in siliciclastic sediments. The tephra layer is medium-well sorted and contains mainly micropumice. This ash layer is underline by a paleosoil layer. According to the  $^{14}\text{C}$  chronology of the paleosoil, the ash layer is  $33.6 \pm 0.8$  ka old or younger. The sedimentological features of the ash layers suggest that they are fallout tephra.

The component analyses of the tephra layers revealed that they consist of predominantly volcanic fragments (>90%) supporting that their primary origin is related to volcanic eruptions and the role of reworking is negligible. The pumice layers (lc1 and lc2) consist of dacitic pumice lapilli (~85 vol%) and mainly lithic clasts of volcanic origin (~15 vol%). Two type of pumice can be distinguished: dense, grey (density > 1 g/cm<sup>3</sup>) and light, white pumice (density < 1 g/cm<sup>3</sup>). They show differences also in the vesicularity and microlite content. The ash layer of locality 3 also contains a high amount of juvenile pyroclasts in form of micropumice (~70 vol%) and crystals (~20 vol%).

On the other hand, the ash layers of locality 2 contain much less amount of juvenile pyroclasts (micropumice and crystals) (~30 vol%) and higher percentage of lithic clasts (~70 vol%). The lower amount of juvenile pyroclasts in these ash layers can be explained by the different eruption type. Pumice and ash layers with high amount of juvenile pyroclasts are likely products of a subplinian-plinian eruption, while the series of ash layers at lc2,

may be the product of a series of phreatic-phreatomagmatic explosions.

The juvenile pyroclasts in all tephra layers have glassy vesicular matrix and are made of euhedral or subhedral phenocrysts of plagioclase > amphibole > biotite and accessory apatite; remnants of orthopyroxene is rarely found in the core of amphiboles. Outstanding result is that Cr-spinel inclusions were detected in the orthopyroxene. The lithic clasts are mainly accessory comagmatic dacitic lava rocks, altered volcanic fragments but accidental fragments (fine grained siliclastic rocks) probably from the basal basement were also found.

The composition of the matrix glass in the juvenile fragments is high K rhyolit ( $\text{SiO}_2$  is between 71 and 78 wt%;  $\text{K}_2\text{O}$  is between 2.2 and 6.5 wt%). According to the composition of the matrix glass and An content of the plagioclase phenocrysts, tephra can be divided into two groups. The pumices in lapilli rich tephra layers (lc1 and lc2) are characterized by lower  $\text{SiO}_2$  and higher CaO,  $\text{Al}_2\text{O}_3$ , FeO in the glass and andesine type plagioclase. In contrast the ash layer of lc3 has higher  $\text{SiO}_2$  and lower CaO,  $\text{Al}_2\text{O}_3$ , FeO in the matrix and oligoclase type plagioclase. Small differences in the MgO, FeO and  $\text{K}_2\text{O}$  characterize the matrix glass of the micropumice in the ash layers of locality 2 and locality 3.

The young age of the tephra at lc3 and the petrographical and geochemical characteristics of the tephra layers clearly indicate that they are the products of the late explosive phase of the nearby Ciomadul volcano. These tephra layers support that the Ciomadul volcano was characterized by different type of explosive eruptions as it was suggested by former authors (e.g.: Vinkler *et al.*, 2007). However, this study detected three different explosive events, indicating that tephra layers in the intermountain basins around the Ciomadul provide a good basis for characterising the explosive eruptions of the volcano.

Preliminary petrogenetic studies on the pumices, including analyses of zoning, texture and geochemistry of plagioclase phenocrysts suggest disequilibrium conditions in the magma chamber before the eruptions. Arrival of fresh magma into the magma chamber might have reheated the system and triggered the eruption related to the pumiceous tephra layers. The arriving magma might have been basaltic, according to the orthopyroxene and Cr-spinel inclusions found in the core of amphiboles.

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## Main types of Ukrainian Shield nepheline rocks: mineralogical and geochemical features

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The Ukrainian Shield (USh) is a classical area of alkaline rocks. Nearly 30 massifs are known in the area, which are situated within the Serebryanoprudniy, Pre-Azov and Dnistrovo-Bugsky blocks of the USh (Kryvdik & Tkachuk, 1990).

This work is selectively devoted to mineralogical and geochemical features of typical USh massifs: Proskurovsky, Antonovsky, Chernigovka, Malotersyansky, Oktyabrsky Massifs and the nepheline rocks of the Gorodnytska Intrusion. Traditionally, such rocks are attributed to two alkaline rock formations: alkaline-ultramafic (carbonatite) rocks of ~2 Ga age (Proskurovsky, Antonovsky, Chernigovka Massifs and Gorodnytska Intrusion) and gabbro-syenite of ~1.7 Ga age (Malotersyansky, Oktyabrsky Massifs). All massifs are mainly located in the shield periphery and confined to extended deep seated fault zones (Kryvdik & Tkachuk, 1990). Host rocks of the Proskurovsky and Antonovsky Massifs are granitoids, host rocks of the Malotersyansky and Chernigovka Massifs are granite, gneiss and amphibolite, while the hosts of the Gorodnytska Intrusion are granite and gneiss. Rocks are considered as a potential source of P, Zr, Nb and REE (Malotersyansky, Oktyabrsky and Chernigovka Massifs) and nepheline-feldspar raw material (Donskoy *et al.*, 2004).

All the nepheline rocks of these massifs are generally represented by nepheline syenites (canadites, foyaites, mariupolites, pulaskites). However, Proskurovsky, Antonovsky and Chernigovka Massifs are also characterized by the presence of ijolite-melteigites and ijolite-jacupirangites. The Gorodnytska Intrusion consists of olivine-nepheline-pyroxene rocks (melanocratic ijolite-jacupirangites are dominated).

All massifs have similar nepheline rock content, but both rock-forming and accessory minerals concentrations vary in a wide range in the different massifs. Main rock-forming minerals are feldspar and albite (40-80%), nepheline (5-50%), amphibole (hastingsite), clinopyroxene (aegirine-salite), biotite (5-20%, up to 40-60% in biotite types), calcite (2-7%), while accessory minerals are apatite (< 0.1-15%), zircon (< 0.1-1%), ilmenite (1-6%) and titanite (0.5-5%). The typical accessories of the rocks of Chernigovka Massif are also pyrochlore (up to 1%) and orthite (0.5%). And there are brytholite, bastnasite, rinkite in the nepheline syenites of the Oktyabrsky Massif (Kryvdik *et al.*, 1990, Nykanorova 2013, Osypenko 2013).

Ijolite-melteigites and ijolite-jacupirangites consist of nepheline (15-65%), feldspars (5-40%), aegirine containing clinopyroxene (10-45%, up to 70% in melteigites), olivine (in Chernigovka – hortonolite 5-20%), amphibole (hornblende and hastingsite 2-10%),

micas (biotite and phlogopite 1-10%). The accessory minerals are apatite (1-3%, up to 5% in Chernigovka), calcite (1-5%), ilmenite and magnetite (3-5%). Besides them, titanite, monazite, phlogopite, graphite and sulphides also occur in Chernigovka (Kryvdik *et al.*, 1990, Nykanorova 2013, Osypenko 2013) and garnet (andradite, melanite), Cr-spinel, albite, rutile occur in the rocks of the Gorodnytska Intrusion (Tsymbal *et al.*, 1997).

However, despite the similarity of mineral composition, geochemical features allow to distinguish separate groups of the rocks of the Proskurovsky and Antonovsky Massifs and the Gorodnytska Intrusion formations. The first one is characterized by low content of such incompatible elements as Nb (3.5-35 ppm), Zr (19-95 ppm) and LREE (10-80 ppm), relatively low TiO<sub>2</sub> concentrations and absence of carbonatites (Dybuna *et al.*, 2011, Tsymbal *et al.*, 2007, Osypenko 2013).

Available Sr, Nd, C, and O isotopic data (Kryvdik 2000, Tsymbal *et al.*, 2007), in spite of the different contamination level by crustal material, indicates mantle origin for this group of rocks. That is why the observed anomalous geochemical specialization of the studied rocks can be explained by different geochemical specialization of their material source, i.e. mantle reservoirs.

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## Major and trace element characteristics of Fe-wehrlites formed by mantle metasomatism beneath the Nógrád-Gömör Volcanic Field (Northern Pannonian Basin)

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There are locations throughout the world where alkali basaltic, lamprophyric or kimberlitic magmas brought ultramafic xenoliths to the surface, which provide unique opportunity to gain direct information about the evolution of the upper mantle. In addition to the dominant lherzolite suite, significant amounts of wehrlite, dunite and harzburgite also appear among subcontinental lithosphere derived rocks, showing different stages of enrichment and depletion geochemical processes.

Assemblages of clinopyroxene-rich ultramafic xenoliths, basically wehrlites, can be interpreted as high-pressure cumulates crystallised from trapped melts near the crust-mantle transitional zone (Frey & Prinz, 1978) or as result of pervasive metasomatism triggered by fluid-peridotite interaction. The ephemeral metasomatic agent of wehrlitization can be carbonatitic melt originating from the deep mantle, producing magnesian wehrlites (Yaxley *et al.*, 1991), or silicic melt forming Fe-rich wehrlites (Peslier *et al.*, 2002).

There are five different locations within the Carpathian-Pannonian region where Plio-Pleistocene alkali basalts enclose great number of upper mantle xenoliths. The northernmost occurrence is the Nógrád-Gömör Volcanic Field (NGVF), where both peridotites (Szabó & Taylor, 1994) and cumulates (Kovács *et al.*, 2004) have been studied, however only cumulative wehrlite xenoliths were announced.

Our study presents a suite of non-cumulate wehrlites owning special petrographic and geochemical features. All wehrlites consist of clinopyroxene-rich and olivine-rich assemblages. The former parts contain tiny rounded olivines (100-200 µm) and vermicular spinel inclusions girdle by irregular shaped, elongated, relatively large (1-3 mm) clinopyroxenes. In coarse-grained clinopyroxenes orthopyroxene remnants can be determined (Fig. 1.). Under crossed nicols, the large clinopyroxenes extinct all at once, implying simultaneous crystallization. The olivine-rich parts can be characterized with coarse-grained olivines having straight grain boundaries and occasionally enclosing rounded orthopyroxenes and minor spinel.

Major element geochemistry of the rock forming minerals was carried out by electron microprobe analyses. As a result, Fe and Mn enrichment in olivines, Ti, Al and Fe enrichment in clinopyroxenes, and Fe and Ti enrichment in spinels can be observed compared to lherzolite xenoliths from the same localities.

Trace element geochemistry of clinopyroxenes in wehrlite xenoliths was determined by LA-ICP-MS analyses and show similar pattern in multi element diagrams for the different localities. The highly incompatible elements, as well as Pb, Hf, and Zr, show strong depletion. Most of the other elements show a flat distribution profile, except for the compatible ones, from which Sc, V, and Cr are slightly enriched, whereas Co and Ni are strongly diminished compared to the primitive mantle. The REY elements

depict a relatively flat pattern with a slight enrichment in such LREE as Ce, Pr, Nd, Sm and Eu.

Summarizing our results, the Fe-wehrlites were formed by an alkali mafic melt-wallrock interaction in the subcontinental lithospheric mantle beneath the NGVF. During this event the original lherzolitic upper mantle went through stealth metasomatism, meaning clinopyroxene is introduced to the system that is mineralogically indistinguishable from common upper mantle peridotites. Together modal variation chemical composition of the rock forming minerals was also changed. Our study provides information on the migrating melts at mantle depths beneath the NGVF in relation to regional geodynamic processes.

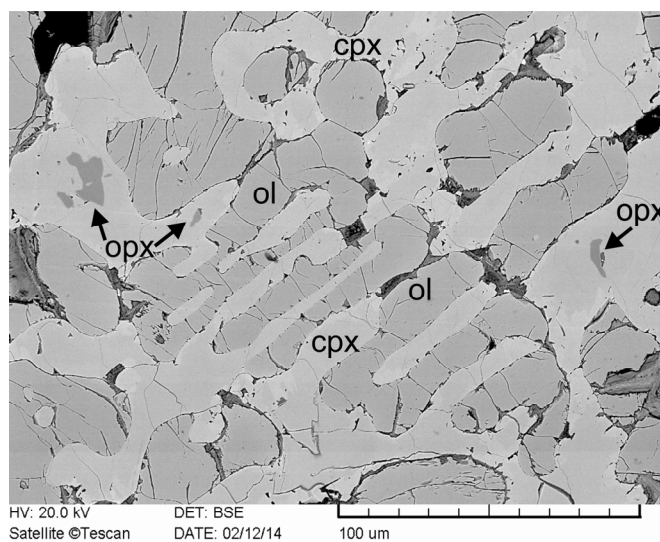


Fig. 1.: Scanning electron microscope image of a clinopyroxene-rich part of a wehrlite with elongated olivine and clinopyroxene grains. Coarse-grained clinopyroxenes contain orthopyroxene remnants (cpx – clinopyroxene, ol – olivine, opx – orthopyroxene).

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## Investigation of marks for deep karstification in the carbonate aquifer system of Buda Thermal Karst

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The hypogenic karst systems are presently less known, in which case the dissolution of carbonates is influenced by deep originated gases, fluids and energy (Palmer, 1991; Klimchouk, 2007). The understanding of these karstification processes is difficult because of the limited access and sampling possibility of this part of rock volume. There is no doubt that the aggressivity of the fluid is responsible for the deep karstification processes but the causes of aggressivity can be hardly investigated (Goldscheider *et al.*, 2010). One of the type areas of the hypogenic karst systems is the Buda Thermal Karst (Fig. 1.).

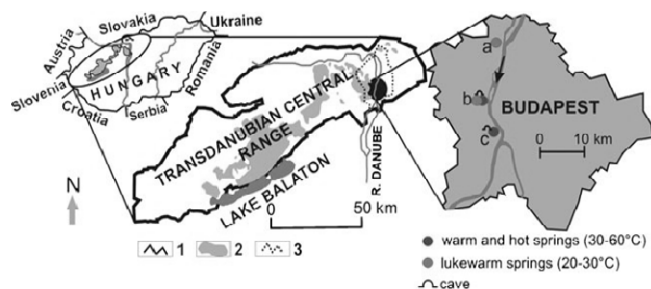


Fig. 1.: Location of the Buda Thermal Karst in the Transdanubian Central Range and the natural discharge areas in Budapest. Legend: 1: Subsurface boundary of Mesozoic carbonates, 2: Uncovered Mesozoic carbonates, 3: Buda Thermal Karst, a-c northern, central and southern discharge areas (Eröss, 2010)

In the understanding of the hypogenic karstification processes the interpretation of geological logs of deep drillings can be helpful. During the work the marks possibly referring to the hypogenic karstification were collected and were inserted to a database. To the documentations 78 water exploration wells were used which were drilled in Budapest and its surroundings, and from these 46 were involved in the evaluation. The marks referring to deep cavities which were taken into consideration are as follows: the presence of the dissolution caves and the fissured sections in the carbonates, the detected mud losses during drilling, and the materials filling out the fissures, such as calcite and argillaceous, silty fillings. In addition, traces of iron-oxide, pyrite precipitates, the presence of stylolite and carbonate rock debris, and the location of supposed faults and structures were also collected which can be also important during the research. The results were displayed on maps (Fig. 2.) and on a geological section in order to determine the location of those sections which are affected by cavities and their relationships with the lithology and the structures.

It could be concluded that mud losses and cavities can occur in all carbonate rocks, even in marls. The correlation of the cavities with structural elements sometimes was detected but in other cases it was not demonstrable. Nevertheless it should be noted that the wells are pointwise and their scale can not be compared with the mapping scale of the structures. Based on the derived maps we determined that cavities can be observed in more well logs from the covered karst compared to the uncovered karst. Taking into consideration the elevation range of the cavities along the section great variability

was found. The occurrence of cavities in the wells extends from some meters to 300-350 metres. In the wells multilevel cavities were found affecting different formations. However there were no cavities effecting both the Triassic and the Eocene formations. Examples from the documentations evidence that pyrite-, iron oxide and calcite precipitates often accompany the cavities in the depth.

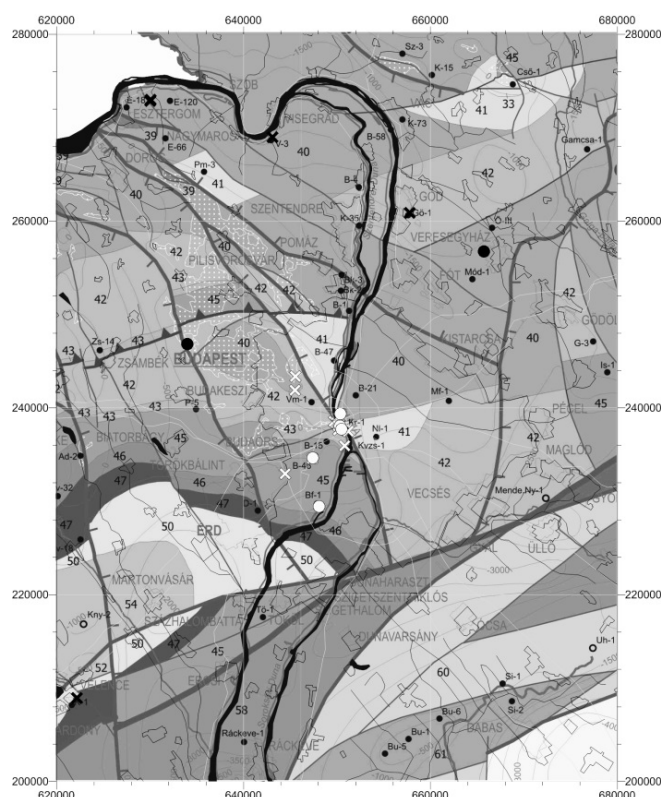


Fig. 2.: Location of the thermal wells drilled in the Dachstein Limestone (black points and symbols x) and the Hauptdolomit (white points and symbols x) and in the previous units occurring cavitation and/or mud losses (points) (Geological map: edited by Haas, 2010)

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The research was carried out for this area within the framework and with the support of the OTKA (NK 101356).

## **Making and using cross-spread domains in 3D seismic processing**

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In hydrocarbon research seismic exploration is the most frequently used geophysical method to find subsurface geological structures. However we need to apply numerous processing steps on the raw seismic data till we can get interpretable sections from the field acquisition. An important part of the seismic processing is the suppression of noise – for example ground roll – for the benefit of the valuable reflections. This paper outlines a special gather of the seismic data the so called cross-spread domain. Utilizing this domain as the input of 3D FKK filter we can reach the suppression of the high amplitude noise caused by the ground roll.

The seismic traces could be sorted in gathers by several ways, depending on the desired processing step. There are many types of gathers for example common depth point gather, common shot point gather or common receiver pointgather. A cross-spread collect determined traces. These traces received by geophones located in the same receiver line, and the sources of these traces are shotpoints located in the same shotline. The shotline and the receiver line must be perpendicular to each other. By this sorting we can get a simple fold gather of traces, which is well sampled and the attributes of the traces – such as azimuth or offset – change in a continuous way trace by trace.

To create cross-spread gathers an orthogonal – the geophone lines and the shotlines are perpendicular to each other – 3D seismic acquisition is required. The raw data of such an acquisition was provided for me by MOL Plc. I selected a smaller part of this data to make a cross-spread gather. The sorting was made by the modules of PROMAX Seisworks. Getting to know the modules and parameterizing them were essential parts of my research and were documented in detail.

The established cross-spreads are appropriate inputs for a 3D FKK filter. By Fourier transformation of the data we can analyse the strength of the signals as the function of three variant, the frequency and wavenumbers of the x and y directions. In this FKK space it is easier to separate the seismic events from each other by their velocities. We can distinguish the slowliest ground roll, the faster direct waves and the fastest reflections. On cross-spreads I tested different velocity filters to suppress the noise caused by ground roll without attenuate the valuable reflections. By comparing the same sections before and after the filtering and analysing the differences of them, the efficiency of the filter can be estimated. I reach the best results at far offsets with using the velocity of the direct waves as the parameter of the velocity filter.

To verify the method I fill the traces of the acquisition with synthetic signals. I created four different seismic events: a reflection, a direct wave and a ground roll which consist of two components with different velocities. I also made cross-spreads from the artificial data volume and used them as input of the FKK filter. The filter show similar results as in case of real data, however in the FKK space strong aliasing effect could be noticed, which can make the distinguish of the seismic events more difficult.

As the result of my research I elaborated a workflow on sorting 3D seismic data into cross-spread gathers and I proved that this gather is an appropriate input for 3D FKK filtering. By this velocity filtering method we can attenuate the noise of the ground roll therefore obtain a better signal to noise ratio and better seismic sections at the end of an overall seismic processing before the interpretation.

## Distribution of nitrates in the groundwater of Svilajnac

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Svilajnac is a city located in central Serbia, with population of about 10 000 inhabitants. The terrain is mostly flat, consisting of alluvial plain located near the confluence of the Resava and Velika Morava rivers. The only hilly parts are river terraces located in the northeast part of the area. The population of Svilajnac is supplied with drinking water from one water supply system, public fountains and individual wells, all of them located in the quarter sediments. Within these intergranular porous rocks, the local aquifer was formed, and it is hydraulically connected with the rivers Resava and Velika Morava. Piezometric level of the wells is generally 3 to 6m below the ground, while their depth is between 8 and 12m.

This research has been done in order to determine nitrate concentration and create maps of nitrate distribution in the region of Svilajnac, by sampling water from 21 sampling point in the period of June-August 2013. Twenty samples were taken from individual wells, and one sample from well that is being used in water supply sistem.. The laboratory tests were done in the Institute „Jaroslav Černi“, Belgrade and in Public communal company „Morava“, Svilajnac, in order to determine nitrate concentration. For creating maps of nitrate distribution in the region, the Surfer programme was used.

It has been determined that the nitrate concentrations in the centre of Svilajnac region and its rim are not equalized. An increased nitrate concentration, above  $50 \text{ mg/dm}^3$ , was found at 6 sampling points which are located on the rim, where one of these sampling points had the maximum nitrate concentration of  $97.24 \text{ mg/dm}^3$  (Fig. 1). This point is more than 790 m away from the Resava and is located outside the area of the city. These grounds are used for keeping cattle and growing different crops, therefore the usage of fertilizers is common. Concentration of nitrates is considerably lower in the central part of research area consisting of the city centre closer to the river. The lowest measured concentration in this part is  $12.40 \text{ mg/dm}^3$ . This is justified considering that the whole population is using this groundwater for drinking.

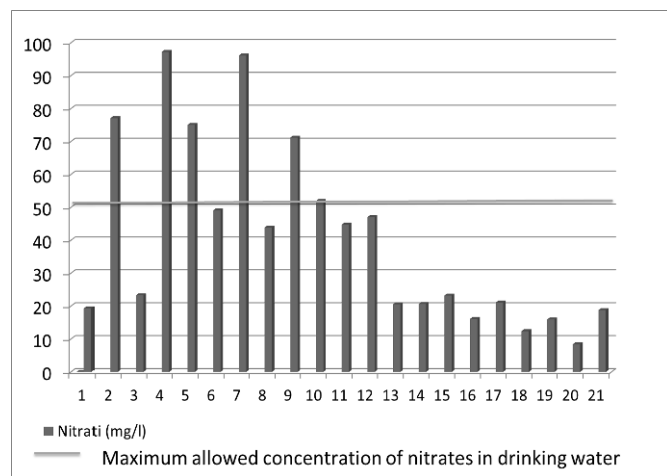


Fig. 1.: Concentration of nitrates at the sampling points

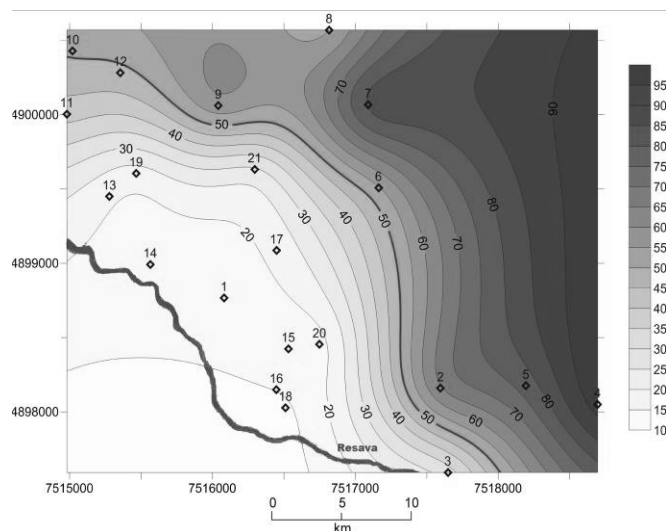


Fig. 2.: Interpolation map which shows distribution of nitrates in the groundwater (squares with numbers are showing the sample locations, while the gray-scaled bar shows the concentration of nitrates)

Interpolation maps showed that the concentration of nitrates is decreasing from the northeast to the southwest of the area, which coincides with the shortening of distance between the sampling points and the river (Fig. 2.).

It is supposed that the increase of nitrate concentration in the rim of the research area is caused by using fertilizers, from which nitrates can be easily infiltrated in the ground. As they cannot stay linked to it, they continue to be infiltrated in the groundwater. According to the terrain relief, the groundwater moves from the hilly to the flat parts – from northeast to the southwest of the research area. During this movement of the water, the nitrates from the rim diffuse, which lead to attenuation of the nitrates and lowering their concentrations.

## Quality of peloids from village Baranda and their use in balneotherapy

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Peloids are geological formations which are made of inorganic and/or organic matter and they are used in balneotherapy (Jovanović *et al.*, 1994). Features of peloids which determine their use value in balneotherapy are absorption, plasticity, viscosity. These three characteristics directly depend on the grain size of the peloids. The dimensions of the most common grains in high quality muds are less than 0.25 mm. Chemical elements that enter into the composition of mud are generally elements, which form rocks. Mechanism of their act in balneotherapy is not enough examined, but it is known that their absorption depends on the pH value. Many spas in Serbia use peloids in medical treatments (Kanjiza, Soko-banja, Gamzigrad Spa). Mud, which we studied, was not analysed before, but residents use it in treatment of rheumatism. This study was conducted with the aim of analyzing balneological features of peloids from the territory of Baranda. Task of the study was to determine chemical and mechanical characteristics.

Baranda is a village in north-eastern Serbia, about 4 km from the municipality of Opovo. It is bordered by the municipalities of Zrenjanin to the north, Kovačica to the east, Pančevo to the south and by the area of Belgrade to the west. Peloids were sampled on two localities; Slatina and Siget (Fig. 1).

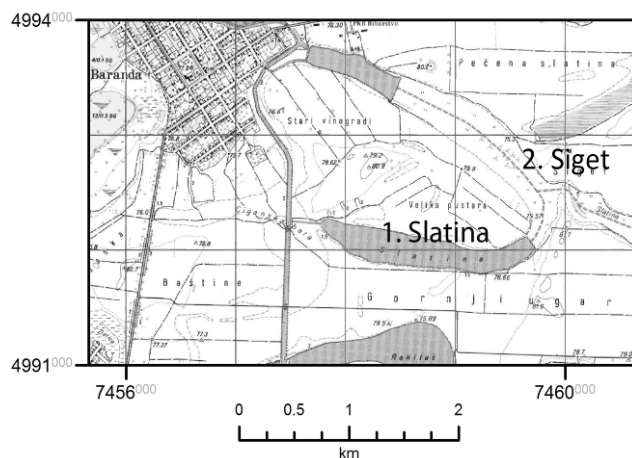


Fig. 1.: Sites of sampling, according to topographic map sheet Zrenjanin 379-4-4, 1:25000

With methods of pH-metry, granulometry, X-ray powder diffraction and atomic absorption spectrophotometry, physical and chemical characteristics of the peloids were determined.

The analysed samples are mildly alkaline, like majority of the peloids from spas in Serbia (Jović *et al.*, 2001). Alkalinity can have positive effect on skin, but it improves precipitation of heavy metals. Indeed, concentrations of heavy metals are less than the average concentration in muds from other sites in Serbia. The presence of Si, Al, Zr, Ca, K, Mn, Ti, Rb and Fe was determined with qualitative analysis. These elements are more or less present in all other peloids from territory of Serbia that Jović studied. But plasticity, which is of crucial importance for balneological value of peloids, is based on its granulometric features. Results of granulometric analysis showed that mud from sites Siget and Slatina are silty sand and sand (Fig. 2.). The grain size of the sand is ranging from 0.05 to 2 mm, which indicates that they are not suitable for use in balneotherapy without prior mechanical treatment, which we could use to homogenize the mud and reduce the grain size.

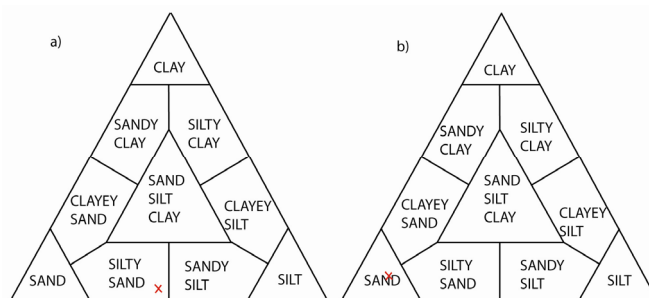


Fig. 2.: Shepard's diagrams; a) Siget, b) Slatina

Despite the relatively positive chemical characteristics, granulometry composition of the peloids from Slatina and Siget prevents their use in balneotherapy without prior treatment.

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## Facies and sedimentation of the Menilite Formation (Lower Oligocene), Skole Nappe, Polish Outer Carpathians

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The Menilite Formation (MF) is a very specific and economically important lithostratigraphic unit of the Outer Carpathians. It is composed of black and brown shale, chert, marl, diatomite, sandstone, breccia and conglomerate occurring in variable proportions. The deposits are both good source rocks and reservoir rocks for hydrocarbons. In the Polish Carpathians, the MF occurs mainly in the outer nappes (Dukla, Silesian, Sub-Silesian and Skole). The deposits show variable sedimentary features making their origin controversial. Clastic deposits of the MF have many specific features not common or rare in other parts of the flysch succession in the Polish Outer Carpathians.

Processes and conditions of sedimentation of the MF deposits and their relationship to the conditions of sedimentation dominant in flysch of the Polish Carpathians have not been precisely explained, yet.

The flysch of the Polish Outer Carpathians is generally considered as deep-water deposit. In contrast, the MF deposits of a marginal part of the Skole Nappe, being the outermost nappe of the Polish Outer Carpathians, are interpreted by some authors as basin slope and shelf deposits. Structures corresponding to hummocky cross-stratification, wave-ripple lamination and wavy to lenticular bedding are indicated to evidence such origination (Jankowski & Probulski, 2011). Anyway, such sedimentary structures can also be developed by hyperpycnal flows. Furthermore, in some parts of the Skole Nappe, diatomite occurs within the MF. It suggests sedimentation in very shallow water (Kotlarczyk & Leśniak, 1990).

Similar deposits were described in Romania. Sedimentation of the MF deposits from the inner part of Tarcău Nappe was interpreted there to have occurred during deepening of the basin (Puglisi *et al.* 2006). These from marginal part of the flysch zone were considered there as resulting from sedimentation by hyperpycnal flows formed in delta systems during catastrophic flood events (Miclăuș *et al.*, 2009).

The author is currently investigating the MF deposits in several sections located in the south-eastern part of the Skole Nappe in the Polish Outer Carpathians (Fig.1).

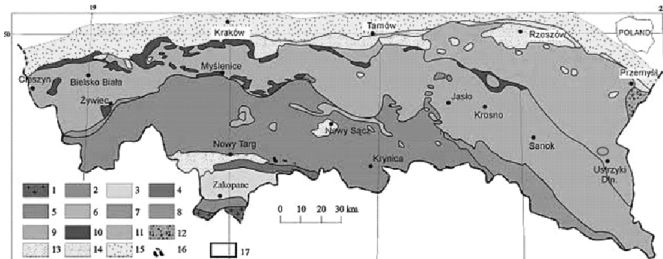


Fig. 1.: Geological sketch – map of the Polish Outer Carpathians with the study area (grey circle, to the right)

The unit is built there of thin-bedded black and brown shale, chert and marl and thin- to thick-bedded, mainly massive sandstone. Some parts of the succession are built of heteroliths displaying wavy and lenticular bedding. Some thick sandstone beds show plane-parallel lamination and ripple cross-lamination in their top parts.

The preliminary data suggest that the thick-bedded sandstones are mass-gravity flow deposits, laid down mainly by high-density turbidity currents, whereas the wavy and lenticularly bedded heterolithic deposits are hyperpycnites. Location of the study area in the inner part of the nappe, together with the thick-bedded mass-gravity flow sandstone, suggest deep-water sedimentation of the entire succession. Occurrence of hyperpycnites implies location of the area in the reach of a big river mouth. Further investigations should significantly improve the interpretations concerning both the sedimentary processes and the nature of depositional system.

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## Organic geochemistry of potential source rocks for shale gas from selected sections of Silurian from Northern Poland

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Potential source rocks for shale gas in Poland, from boreholes Darżlubie IG-1, Prabuty IG-1 (Baltic Basin) and Tuszcz IG-1 (Podlasie Depression) were examined to identify biomarkers and molecular parameters of maturity. The analysed black, quartz–mica (muscovite, chlorite) shale of Wenlock–Ludlow age contain small amounts of organic matter (<1% TOC). Samples from Llandovery, containing 1.6–14.0% TOC, seem to be a good source rocks.

Detailed analysis of the organic matter was performed, including the extraction of bitumen, the extracts separation into fractions and molecular analysis. *n*-Alkanes, acyclic isoprenoids: *nor*-pristane, pristane and phytane, alkyl-naphthalenes, phenanthrene and alkylphenanthrenes, chrysene and alkylchrysenes, fluorene-9-one and alkylfluorene-9-ones were identified. The only identified biomarkers, *nor*-pristane, pristane and phytane, indicate that organic matter origin from phototrophic organisms. The distribution of short-chain *n*-alkanes and rapid decrease of the higher homologues (Fig. 1.), suggest high maturity of the organic matter, altering the initial distribution of *n*-alkanes by diagenetic/catagenetic processes, however, such distribution can also be a signal from microbial-algae bioprecursor.

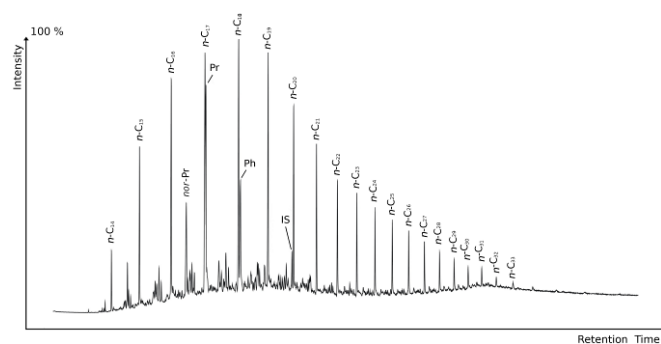


Fig.1.: The total ion current (TIC) chromatogram for sample DAR\_1Ap (column HP-5MS); IS – Internal Standard: eikoz-1-en, *nor*-Pr – *nor*-pristane, Pr – pristane, Ph – phytane.

Distribution of dimethylphenanthrenes is consistent with the marine origin of the organic matter, also indicated by the presence of conodonts. A bimodal distribution of *n*-alkanes in one of the samples, with a second maximum for long-chain molecules, may indicate the existence in Silurian other than higher plant precursor of long chain *n*-alkanes, or bitumen mixing with hydrocarbons from younger rocks containing a component of higher plants. The rocks of Llandovery and middle Ludlow ages show high trimethylphenanthrene content, specific for some Paleozoic rocks, which can be used for age correlation in a wider area.

The absence of common biomarkers, except the most thermally resistant pristane and phytane, suggests maturity of organic matter above  $R_r=1.1\%$ . It is consistent with the maturity estimated from the recalculation of the molecular maturity parameters values (CPI, MPI-1, DMPR, MPR, MCHR, 2-MChy/1MChy) into calculated vitrinite reflectance ( $R_c$  0.66–1.19%), corresponding to oil window ( $R_r$  0.5–1.2%). This suggests that in the analysed rocks primary thermogenic gas could be generated in small amount but generation of secondary thermogenic gas is unlikely.

However the resulted  $R_c$  values may be misleading, due to the fact that the relationships between molecular maturity parameters and calculated vitrinite reflectance (e.g., Radke & Welte, 1983; Cassani *et al.*, 1988; Li *et al.*, 2012) were developed for kerogen Type III, while the studied samples contain Type II kerogen. Degree of maturity of the samples containing Type II kerogen must be therefore confirmed by other studies, e. g., by measuring the Conodont Alteration Index.

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## The temperature conditions of epigenetic mineralization formation in Ratno Beds within Rafalivka area (Volhyn, Ukraine)

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The Ratno Beds, a part of Upper Proterozoic flood basalts formations, is, located in the Volhyn (Ukraine) (Shymlyansky, 2006, Bialowolska *et al.*, 2002, Derevska, *et al.*, 2008). The Ratno Beds within Rafalivka ore-bearing area consists of one to four basalt flows which are interbedded by tuffs, tuffbreccias and lavobreccias. Mineralogical and petrographic study of volcanic rocks and their postmagmatic alterations show that basalts differ in their rock-forming minerals quantity and secondary alterations, structural and textural parameters, the presence of amygdaloids, veins and voids. Epigenetic mineralization in the Ratno Beds is represented by palagonite, chlorite, zeolite, analcime, opal, chalcedony, iron hydroxide, carbonates, quartz, barite, wairakite, iron- and copper sulphides etc. Native metals are represented by native copper (main ore mineral), silver, iron, nickel etc (Rudenko *et al.*, 2013).

At the beginning of the 21st century, more than 200 boreholes were drilled within Rafalivka area (Chartoryisk fracture zone) and comprehensive geological and geophysical exploration with the goal to find native metals were conducted. Being highly explored this area was relevant for detailed studies and for clarifying thermobarogeochemical conditions of secondary mineral formation. About 50 mineral samples (quartz, calcite, analcime) from the Ratno Beds were selected and analysed by gas-liquid inclusions (GLI) homogenization method. These minerals were taken from the amygdaloids, veinlets, breccias cement and so on.

Earlier, the temperature of epigenetic mineralization formation and the sequence of mineral-forming processes in the volcanic section of the Rafalivka area were determined as result of thermobarogeochemical research. It was shown that the maximum temperature of the epigenetic mineralization was 335°C (from wairakite and quartz). This high temperature was resulted, presumably, by some additional heat source which appeared after the cooling of the basalt flow and the formation of an autometasomatic mineralization at temperature 100-50°C. The most favourable temperature for the native copper formation is 175-125°C.

Our additional studies within a chosen polygon displayed, that epigenetic minerals were formed at low temperatures between 150-100°C (Fig. 1). It should be noted, that wairakite, which was recorded in other wells in the western part of Rafalivka area, was not found among the newly formed minerals. Since wairakite is the high-temperature hydrothermal analogue of analcime, it forms at 175-400°C. This fact may also confirm low-temperature nature of the epigenetic mineralisation within the research area.

Taking into account our data and the results of previous studies (Derevska *et al.*, 2001), we constructed a contour diagram which shows the maximum temperature distribution of homogenization GLI of quartz and analcime for Rafalivka area (Fig. 1).

Two temperature-zones of epigenetic mineralization formation are determined in Rafalivka area within the Chartoryisk fracture zone. The first one (150-335°C) is a high temperature zone, which

is indicated by wairakite (200-335°C) and quartz (150-300°C). Analcime, chlorite, zeolite, native copper, silver, iron etc, are also abundant in this zone. The second zone is of low-temperature (125-100°C). It is allocated between the major lineament of the Chartoryisk fracture zone (near Polytsi quarry). The temperatures were estimated by quartz and analcime. In this case, the mineral association is represented by quartz, barite, opal, chalcedony, calcite, native silver, iron and copper sulphides. The distribution zones of the low-temperature mineralization confined elevated concentrations of gold.

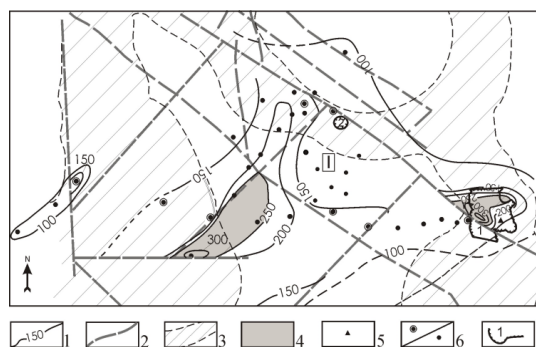


Fig. 1.: Scheme of temperature maximum values variability of gas-liquid inclusions homogenization in quartz, wairakite and analcime (modified after Derevska *et al.*, 2001). 1 - isolines of homogenization temperature maximum values; 2 - faults; 3 - magma-controlling zones; 4 - homogenization temperature values over 250°C; 5 - place of copper nuggets discovery; 6 - drillholes, which copper content > 0.1% (a) and other drillholes (b); 7 - quarries: 1 - Rafalivka quarry and 2 - Polytsi quarry. I - study area.

Thus, in the east Rafalivka area within the Chartoryisk fracture zone the high-temperature processes of mineral formation were not revealed. That is shown by the absence of wairakite and a significantly lower temperature of the mineral (analcime, quartz, opal, chalcedony, etc.) formation. These data may indicate the distance of the research area from the additional heat source, which existed in the central Rafalivka area during the epigenetic mineralization of the Upper Proterozoic Ratno Beds.

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## Silicification of the Upper Jurassic (Oxfordian) deposits of Kraków area

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The area of Kraków is located in southern Poland, in the most southern part of the Kraków-Częstochowa Upland. It mainly consists of Oxfordian limestone of three structural types: platy limestone, bedded limestone and massive limestone. Also certain types of silicification have been found in that rocks, especially cherts are commonly found in the bedded limestone. Silicification was mainly described during other lithological studies, barely in a separate paper and individual researchers have used different nomenclature and divisions. Rajchel (1971) collected the summary of the current knowledge on the Oxfordian silicification, however, by introducing their own names. Nevertheless, several common types of silica can be described in deposits of the Krakow area:

A) Cherts – the most common type of silica present in bedded limestone. They occur as siliceous nodules with sharp boundaries, their typical features are the absence of porosity, chocolate, dark-brown or gray color, diameter < 15 cm and a crystallinity index of < 1. Cherts appear in interlayered horizons (Matyszkiewicz, 1989; Matyszkiewicz, 1996) or completely chaotic. This may be related to the presence of primary clay mineral horizons, where silica has formed concretions. That kind of silicification represents early diagenetic changes and their origin is connected to pH changes. Sponges rot in anaerobic conditions (results of sulphides from seawater reduction) and can be a reason for pH increase and the dissolution of silica. Spicules of the sponges are probably the main source of the silica (Pawlikowski *et al.*, 1978).

B) Silicified limestone – occurs inside bedded limestone as layers of about 0.4 m thickness and a length of up to several meters, it is characterized by sharply separated zones of silicification and the presence (or absence) of carbonates and a crystallinity index ~5.1. The origin of this type is probably also early diagenetic.

C) Irregular nodules – Alexandrowicz (1960) described a rare, small, porous, gray, irregular concentration of silica of unknown origin, which presents in the rock together with common chert (Matyszkiewicz, 1989). They can be seen on the erosion prepared surfaces or by dissolving the rock samples with a hydrochloric acid.

D) Epigenetic Silicification – presents in almost all Kraków area outcrops. Mainly regardless of lithology, it occurs in the top of the Upper Jurassic deposits. This type is porous, gray or pale brown, always has unequivocal boundaries with the surrounding rock. In this case, the limestone is hydrothermally replaced (Rajchel, 1971; Matyszkiewicz, 1987) by silica (90%). Very high degree of crystallinity is common, in the range of 9.2 to 9.9 (Matyszkiewicz, 1987), suggesting a total lack of chalcedony and opal. The time of replacement is unknown, probably younger than Santonian (Alexandrowicz, 1958). The source of the silica is also not exactly known. It could be the dissolution of spicules (Alexandrowicz, 1958) or the primary component of the hydrothermal solution (Matyszkiewicz, 1987).

Geological fieldwork took place in the Piekary outcrop, where the rock wall height is about 16 metres. In the northern part of the quarry occurs the bedded limestone with clearly visible 0.9-2.5 m thick layers with flints, while in the southern part massive limestone occurs.

Quantitative research shows that the bedded limestone contains up to 6.5 % chert and circa 8.33 % of sponge skeletons. As a contrary, massive limestone contains only 7.33 % of sponge skeletons.

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## Geological exploration in the area of Zeleni vir (Green Whirlpool) and Vražji prolaz (Devil's Passage) (Skrad, Croatia)

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In the area of Gorski Kotar (Croatia), within Skrad municipality, the protected landscape Zeleni vir/Vražji prolaz (Green Whirlpool/Devil's Passage) is located. Since 1962 this area is protected and classified as a geomorphological reserve and since 2011 it is protected and classified as a protected landscape.

Specific geological characteristics of the protected landscape Zeleni vir/Vražji prolaz area were the main reasons for starting a *Geological educational trail project*, which was initiated by the tourist office of Skrad municipality. The main goal of the project is to display the geological features of the area to the numerous visitors of this protected landscape and to explain them geological processes and events involved in its formation.

Zeleni vir/Vražji prolaz area belongs to the mountain range of the Outer Dinarides, which is built mainly of Mesozoic and Palaeogene carbonate rocks. According to the basic geological map (1:100 000), Delnice sheet (Savić *et al.*, 1983), clastic rocks of Permian and Triassic age are also present in the Zeleni vir/Vražji prolaz area. However, lithostratigraphical and structural relationships are not clearly visible within the scale of the map. Therefore, construction of the more detailed geological map of the area is the main goal of the project, together with a geological reconstruction and a lithostratigraphical and structural revolution.

Research started in the summer of 2013, as an independent student project, logistically supported by Skrad municipality. Initial field work resulted with definition of the research area and with the main lithological and stratigraphical description of rocks outcropping within the area (Lower- and Middle Jurassic dolomite and limestone, Upper Triassic dolomite and clastic rocks of still questionable age - Triassic and/or Permian). Therefore, representative samples of these clastic rocks (mainly sandstone, but also siltstone/mudstone and fine conglomerate occur) were taken for petrographic microscopic analysis and analytical procedures aimed to define the lithological and stratigraphical characteristics. Carbonates (dolomite and limestone) are also systematically sampled throughout the research area and submitted to micropetrographical and palaeontological analysis.

Furthermore, structural relationships of grandiously-folded Jurassic carbonates were investigated. Main problems of folding mechanisms and the timing of structural deformations are questioned and they are still under discussion. Several structural models and scenarios are proposed. Some stratigraphical determinations are missing (because of the lack of fossils within some of the sampled rock packages), which further complicates the proposed structural model and the exact timing of the geological events.

Vražji prolaz (Devil's Passage) is actually the canyon insisted by Jasel Stream within Jurassic carbonates. According to our results of the geological field-observations and structural measurements, development of the canyon is initiated by faulting of carbonates, followed by spreading the fault zone and accelerating dissolution and weathering of carbonates. Differences in the lithology and

structural relationships in the two opposite canyon walls are clearly visible, indicating major faulting movements.

Additional geological and morphological features, which are also valuable components of the protected landscape Zeleni vir/Vražji prolaz (Green Whirlpool/Devil's Passage), are the small (cca. 200 m long) cave called „Muževa hišica”, with a constant air-temperature of 8°C throughout the whole year and the karst spring called Curak, situated at the contact of folded Jurassic carbonates (Fig. 1) and underlying carbonates. High discharge at the spring and its high hidropotential is used for a power plant called „Munjara” built already in the year 1922.

The results of the *Geological educational trail project* will be submitted to compete for University of Zagreb Rector's Award and this research will also result in two MSc thesis works:

1., I. Gudac will describe and interpret petrological and lithostratigraphical characteristics of clastic and carbonate rocks within the research area (under the supervision of prof. U. Barudžija).

2., M. Sećanj will describe and interpret structural relationships within the research area (under the supervision of prof. B. Tomljenović).

Also, they will help to better understand the hidrogeological and geomorphological open questions within the area of Zeleni vir/Vražji prolaz (Green Whirlpool/Devil's Passage).



Fig. 1. Folded Jurassic carbonates

Savić, D., Dozet, S. (1980): Basic geological map of SFR Yugoslavia (1:100 000), Delnice sheet

## Geochemical modelling the effect of CO<sub>2</sub> injection on the Szolnok Sandstone Formation, Hungary

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One of our extensive environmental problems is the global climate change and its impact on Earth ecosystems that we can all feel on our own skin. Therefore, mitigation of anthropogenic greenhouse gas, most importantly CO<sub>2</sub>, emission is one of the main challenges of humanity. Carbon capture and geological storage is considered to be an efficient technology in eliminating carbon-dioxide at large, stationary carbon-emitting industrial sources. To ensure the long-term stability of the geologically trapped CO<sub>2</sub>, behavior of system of the CO<sub>2</sub> reservoir rock – pore water should be predictable on geological timescales.

In Hungary the best candidate for CO<sub>2</sub> storage is the mostly saline aquifer of the Great Hungarian Plain (SE-Hungary), with sandstone reservoir and clayey caprock. The Neogene basin of the Great Hungarian Plain was subsided and then filled by a prograding delta system from NW and NE during the Late Miocene, mostly in the Pannonian time. The most potential storage rock was formed as a fine-grained sandy turbidite interlayered by thin argillaceous beds in the deepest part of the basin. It has relatively high porosity, depth and more than 1000 m thickness. Providing a regional coverage for the sandy turbidite, a 400-500 m thick argillaceous succession was formed in the slope environment of the delta. The composition, thickness and low permeability is expected to make it a suitable, leakage-safe caprock of the storage system (Falus *et al.*, 2011).

The major question in the CO<sub>2</sub> geological storage is the geochemical behavior of the potential storage rock – pore water – CO<sub>2</sub> system, hence the processes in the reservoir taking place in geological timescale. For this reasons, to obtain a realistic picture about the geochemical behavior of the potential CO<sub>2</sub> storage system, geochemical models were developed for the reservoir rocks. The PHREEQC 3.0 code (newest version from Parkhurst & Appelo, 2012) was used to derive the equilibrium and kinetic geochemical models applying the internationally accepted *llnl.dat* thermodynamic database, which is based on the data of Lawrence Livermore National Laboratory (USA). The data used in the models are actual, measured pore water compositions and an average mineral composition of the possible reservoir rocks, called Szolnok Sandstone Formation.

To determine the rock composition used in the models, drilling core samples have been collected from the potential reservoir rock in the Great Hungarian Plain. Thereafter thin sections were made to define their modal compositions, pore distributions, pore geometry and grain size. To obtain more accurate modal composition, petrographic observation, SEM analyses, XRD and Thermal Analysis (TA) measurements have also been carried out. The water compositions of the studied depth were known from well-log database. Using the information, acquired from these archive

documents, we have constructed input data for geochemical modelling.

The results of the equilibrium model indicate decreasing pH during the dissolution of CO<sub>2</sub> into the pore water. Furthermore show complete dissolution of albite, chlorite and kaolinite and partial dissolution of calcite, K-feldspar and pyrite. In addition precipitation of the following phases also takes place: quartz, muscovite, dolomite, ankerite and as a new phase dawsonite (NaAlCO<sub>3</sub>(OH)<sub>2</sub>) (Fig. 1.). The latter plays a key role in mineral sequestration of CO<sub>2</sub>.

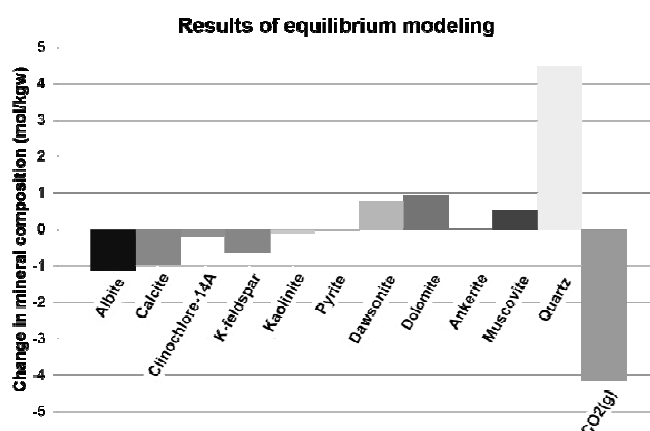


Fig. 1.: Changes in mineral composition of the potential Szolnok Sandstone Formation storage rock as a result of the injected CO<sub>2</sub>. For further explanation see the text above.

Furthermore, the kinetic models, which provide a time/rate dimension to the observed reactions, suggest that the dissolution of calcite and precipitation of dolomite and ankerite are rapid reactions considering the time scale of CO<sub>2</sub> storage. Additionally, it can be assumed that the dissolution of albite plays an important role in dawsonite formation, as source of the necessary Na<sup>+</sup> and Al<sup>3+</sup> content.

Our geochemical models can contribute to better understand the reservoir behaviour in response to future CO<sub>2</sub> injection, therefore more efficiently reduce geology related risks in CO<sub>2</sub> storage.

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## Study of a peperitic basalt occurrence of the Vardar-zone (Doboj-Jug, Bosnia and Herzegovina)

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The surrounding area of the Bosanski Ozren Mountain in northern Bosnia and Herzegovina is a tectonically complex region. The Zagreb-Tuzla line is situated in this terrain, which separates the two former oceanic branch of the Balkan-peninsula: the Dinaridic Ophiolite Belt and the western belt of the Vardar Zone (Karamata, 2006). These belts consist of two fundamental allochthonous components; the ophiolitic mélange and the variably dismembered, mainly ultramafic-mafic bodies related to ophiolitic series. The massif of the Bosanski Ozren was previously listed among the mafics of the Dinaridic Ophiolite Belt, but nowadays it is considered to be the part of the adjacent Vardar Zone western belt (Bazylev *et al.*, 2006; H. Hrvatović, pers. comm.). A locality next to Doboj-Jug with Triassic peperitic basalts was studied. It is situated west from the ultramafic body of the Bosanski Ozren, probably in its accretional mélange. This rock suit shows several similar textural features to the well-known peperitic basalt occurrences of the Dinaridic Ophiolite Belt (Kiss *et al.*, 2012). As by far the presence of the peperitic facies in Doboj Jug was not evidenced, one of the main aims of this project was to prove it.

The Triassic extrusive mafic succession and the coupled sedimentary rocks are studiable in a 40 m long outcrop, and are interpreted as part of a subaqueous basaltic lava flow with two main volcanological facies. The first is a greenish, spilitised, closely packed pillow facies which is in contact with the second, reddish siltstone, marlstone, mudstone and reddish grey basalt containing rock suit along a tectonized zone.

Petrological examination of the basalt of each facies showed intersertal texture and a strong hydrothermal alteration. However, this alteration is more intense on the peperitic facies. Both basalts consist of hipidiomorphic albitized plagioclase, cracked pieces of pyroxene with diopsidic core and augitic rim, idiomorph ilmenite, limonitized hematite and mainly chloritized groundmass. Furthermore, frequent calcite veins and iron-bearing secondary mineral rims around the pyroxene grains could be found in the reddish grey basalt. According to the similar mineralogical composition and textural features, both basalts have a similar origin, i.e. are most likely comagmatic.

The studied clastic sedimentary rock, which occurs together with the reddish grey basalt, was siltstone. This rock consists of mica and well-rounded quartz grains and contains albite fragments identical to the ones found in the basalt, thus their appearance can be

interpreted as a result of the lava-unconsolidated sediment mingling, i.e. the presence of the s.s. peperitic facies.

Chemical analysis of the pillow basalt resulted in slightly high MgO, P<sub>2</sub>O<sub>5</sub>, Na<sub>2</sub>O, TiO<sub>2</sub> and lower FeO, CaO and K<sub>2</sub>O concentration compared to average MOR basalt samples (Wilson, 1989). The peperitic facies is more enriched in CaO and K<sub>2</sub>O, most likely because of the presence of the sediment. The rather high MgO content of the closely packed pillow basalt can be the result of the more intense chloritization. The bulk rock analyses, as well as the composition of the clinopyroxene crystals show petrogenetical conditions related to oceanic island alkali basalt volcanism.

Though macroscopically several similarities were found, the characteristics of the Triassic, Neotethyan rifting related peperitic basalt occurrences of the Dinaridic Ophiolite Belt (Kiss *et al.*, 2012) differ from the studied ones. As a contrary, several similarities can be observed with the peperitic basalt occurrence of the Kozara Mountains, which formed related to the opening of a Cretaceous back-arc basin in the western belt of the Vardar Zone (Grubić *et al.*, 2009; Ustaszewski, 2009). In spite of the observed similarities, the age and the geotectonic position contradict this relationship. Thus, finding evidences to an oceanic island type, subaqueous alkali basalt volcanism coupled with peperitic basalt facies shows us a new episode of the evolution of the Vardar Zone during the Triassic time.

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## Supergene Processes in the Copper Mineralization at the Kraljičin Zdenac on the Medvednica Mt.

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Supergene leaching, oxidation and chalcocite enrichment is a common process which takes place in the weathering environment of copper mineralisation. Penetration of oxygen rich water under the earth surface, is a beginning of a new geochemical scenario which changes hypogene parageneses into a garden of numerous supergene minerals, with an astonishing lush of flashing colours.

Eh-pH diagram of the stability fields of common supergene sulphide and oxide minerals in the system Cu-C-S-H<sub>2</sub>O (Fig.1) shows possible paths followed by solution descending from the oxidized zone, generating enrichment, and infiltrating into hypogene ore or protore. The facies are defined by hydrologic regimes in the vadose zone, in the zone of capillary fringes and in the saturated zone.

Sulphide oxidation takes place above the water table as an electrochemical process mediated by acidophilic, Fe- and S-oxidizing bacteria. Prevailing acidic condition facilitates leaching of Cu, which is transferred downward to the reduced environment, beneath the water table, where sulphide enrichment takes place. Enrichment is primarily an abiotic cation-exchange reaction of Cu, which substitutes more electronegative metals. The required S is inherited from the replaced sulphide minerals. Bacteria also play a role in the enrichment process by facilitating metal adsorption.

Primary mineralization consists of stratabound ore body within a parametamorphic rock series. The ore layer is "sandwiched" between hangingwall metadolostone and the silicified layer of protomarl as a footwall. Primary minerals are chalcocite, pyrite, and eventually primary bornite. The gangue minerals are anhedral quartz, carbonates, and barite.

The shape of the secondary copper mineralization at Kraljičin Zdenac is a pseudo-layer approximately 1 m thick, with (A) pyrite and (B) chalcocite-pyrite rich area.

Supergene processes in this restricted space, developed a faint zonation that could hardly be compared with the standard architecture of the supergene oxidation and enrichment zones above a primary Cu mineralization above an appreciable ore deposit. The common zoning in an ideally developed supergene cover, from the top to bottom is: leached cappings (gossan cap), oxidized Cu ore, and chalcocite-enriched ore (cementation zone, Sillitoe, 2005). The ore outcrop at the Medvednica Mt. contains three assemblages, characteristic of the oxidizing supergene process: (i) Mild oxidation stage; primary ore containing chalcocite and pyrite, and bornite mildly oxidized into covellite (ii) Moderate oxidation stage; moderately oxidized ore containing chalcocite, covellite, and copper oxides, and native copper (iii) Intensive oxidation stage; intensely oxidized ore containing chrysocolla, azurite, malachite and goethite.

Chemical thermodynamics invoked geochemistry as an unavoidable tool in quantitative interpretation of complex natural systems. Among various thermodynamic stability field diagrams the Eh-pH ones have been found most convenient for describing mineral-solution equilibria in near-surface environments. Their

accuracy greatly depends on the consistency of standard free energy data. There is no easy guide to estimate their validity. Their estimation goes far back in the middle of the past century. Some useful criteria to choose reliable ones is the frequency of their use, and persistently similar values coming from different sources. The Eh-pH diagram, constructed for use in this research, is a rectification of the earlier ones (Garrels, 1954; Garrels & Christ, 1965; Sikka *et al.*, 1991, Sato, 1992) (Fig. 1.). The oral presentation brings a thermodynamically up-to-date Eh-pH diagram of copper species in the system Cu-S-C-H<sub>2</sub>O.

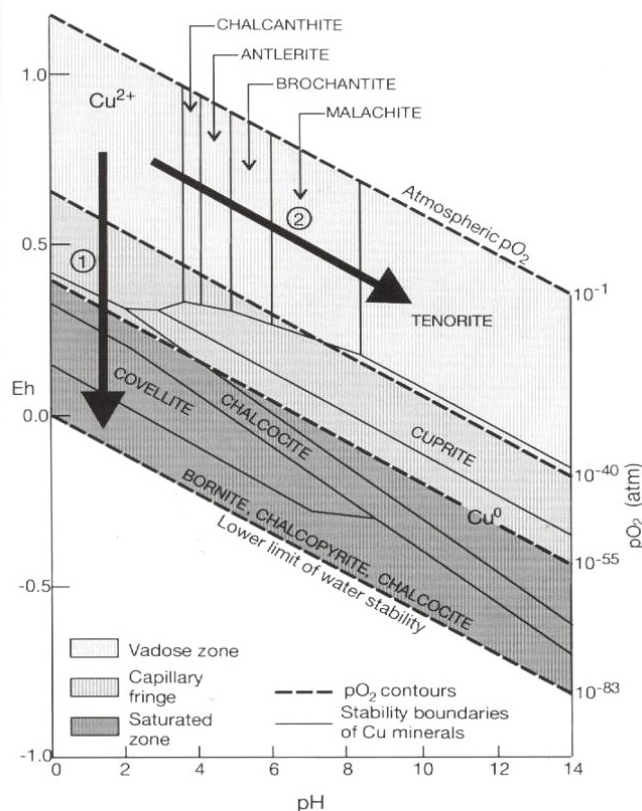


Fig.1.: Eh-pH diagram for supergene copper mineral species in the weathering environment (Garrels, 1954; Garrels & Christ, 1965; Sikka *et al.*, 1991, Sato, 1992).

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## **Geothermobarometry of micaschists with staurolite (Crni Vrh - Serbia)**

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Micaschists, that are characterized by very large staurolite porphyroblasts reaching up to 10 cm in size, occur in the southwestern part of the Paleozoic crystalline complex in Serbo-Macedonian massif at Crni Vrh (in the vicinity of Bagrdan). Beside quartz, mica (muscovite and biotite) and staurolite, these micaschists contain garnet porphyroblasts up to 0.5 cm in size and a smaller amount of plagioclase, too. Accessory minerals are tourmaline, ilmenite and apatite, while secondary chlorite also occurs.

Micaschists display porphyroblastic texture with some lepidoblastic character. Staurolite occurs in the form of euhedral to subhedral grains, in which the inclusion of quartz and mica are common. According to its chemical composition, the investigated

staurolite is nearly an ideal ferruginous hydrated aluminosilicate with a relatively low magnesium content ( $\text{MgO} = 0.2\text{-}1.5\%$ ).

Euhedral garnet porphyroblasts also contain inclusions of quartz and mica. According to its chemical composition, the garnet is generally 65-73% almandine with 12-18 % pyrope component but a smaller amount of spessartine component (5-8 %) also occurs, whereas the contents of grossular and andradite are negligible.

The average temperature of metamorphism for these micaschists, calculated on the base of garnet – biotite geothermometer is  $580 \pm 50^\circ\text{C}$ . According to the garnet – plagioclase – kyanite – quartz geobarometer, the obtained pressure is  $6.1 \pm 0.5\text{kbar}$ .



## Structural analysis of neotectonic activity in the Lonja-Ilova basin between Daruvar and Kutina (North Croatia)

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The study area is located in the western part of Slavonia, at the centre of the Ilova Basin between Daruvar and Kutina in northern Croatia. In geotectonic view, the studied area is located on the southern edge of the Tisia Megaunit, some 10 km north from the Sava-Vardar Zone (Pamić, 2002). Due to the uplifted morphostructure of the Papuk Mts., the hydrographic network is well developed: short streams at the northern slopes of the area drain to the Drava Basin, while streams at the southern slopes drain to the Sava Basin.

According to the opinion of various authors, the current position of the Slavonian Mountains is a result of multiple tectonic movements and rotations during the Miocene. This assumption is supported by detailed facies analysis of semi metamorphic younger Paleozoic and Mesozoic formations within the Tisia Megaunit (Kovács *et al.*, 1989), indicating that the crystalline complex of the Slavonian Mountains should be palaeogeographically linked to the northern margin of the Tethys. This is also consistent with the correlation of the ransgressive Mesozoic sediments, which was described by Šikić *et al.* (1975). The final uplift of the Slavonian Mountains is related to the Tertiary evolution of the Pannonian basin, which is according to Pamić & Lanphere (1991) related to the period of tectonic inversion during the Pliocene and Quaternary.

The aim of this work was to analyse surface and subsurface structures related to neotectonic and on-going tectonic activities. Fourteen reflection seismics sections – in total length of 303.42 km over a surface area of 484.58 km<sup>2</sup> arranged in NW-SE and NE-SW oriented grid were analysed using Petrel 2010 software. Time-depth structure contour maps were constructed using four stratigraphic horizons: the base Tertiary, the base Pannonian, the base upper Pontian and the base Pliocene-Quaternary. Morphometric analysis was done based on the digital elevation model (DEM) with 25-m resolution, analysed with ArcMap 10 tools.

The structural analysis indicated two neotectonically active faults: the Dežanovac and the Daruvar reverse faults, accompanied by kilometre-scaled anticlines in their hangingwalls. According to

their geometry, these are classified as *fault-propagation folds*. The magnitude of their displacement vectors varies from 800 to 350 m, which corresponds to the slip rate of 0.069-0.030 mm/year. The geomorphological analysis was carried out with the quantitative -relief and slope angle and qualitative morphological data-characteristics of drainage network; obtained from 21 catchment areas. Comparing with the data obtained by interpretation of reflection seismics and DEM-based morphometric analysis, it can be concluded that the subsurface structures have a direct expression on surface morphology and on drainage network, too. However, these can be found only locally, in cases, where fault slip rates and tectonics uplift exceeds the rate of erosion and denudation.

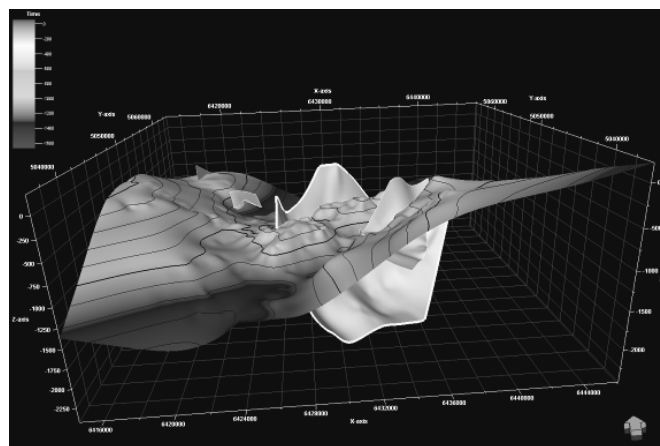


Fig. 1.: 3D surface horizon of Tertiary base with fault plane.

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## More than 300 km raft on the ice floe. Dumortierite and clinohumite from the Bohemian Massif in Dunavarsány, Middle Hungary

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The glaciations events and the periods between them during the Pleistocene caused a big surface shaping effect in the Carpathian-Pannonian region. In the higher topographical regions, the erosion had a greater effect, so the debris transported downwards and accumulated on terrains with lower relief (basins, plains). The origin of the pebble assemblage on the plain south from Budapest can be explained with the same process. From the end of the 19<sup>th</sup> century, the proper way of transport, the structure and composition of terraces has been studied. Getting known about these processes, the surface-forming behaviour of the fluvial systems and climate conditions of that age can be revealed. Petrographic examination of pebbles and boulders is an excellent way to find the source area of fluvial debris. The place of origin of unique rocks with lower abundance can be better located.

In the gravel pits around Dunavarsány the upper Pleistocene alluvium of the Danube is mined intensively. This formation can be well located: under these fluvial sediments there are Pannonian limnic and swamp formations with the complete lack of coarse-grained alluvium. Meanwhile, thin Holocene sediments cover the area. The alluvium in the vicinity of Dunavarsány belongs to the Csepel Member of the Pestvidék Pebble Formation. Why is this pebble formation interesting? It contains mainly (more, than 90%) classical fluvial-formed coarse-grained pebbles, but there are some bigger (even more, than 1 m in diameter), sometimes almost completely angular blocks in it.

Two special rock types from the latter range are in the centre of our research. In each of these rock types, we described characteristic minerals, which have been unknown from Hungary before. The clinohumite (general form:  $\text{Mg}_9(\text{SiO}_4)_4(\text{OH},\text{F})_2$ ) was found in one dolomitic marble block in which besides clinohumite calcite, dolomite, olivine, spinel, apatite, tremolite, chlorite and phlogopite appear also. The other key mineral is the dumortierite

(general form:  $\text{AlAl}_6(\text{BO}_3)\text{Si}_3\text{O}_{13}(\text{O},\text{OH})_2$ ) which was detected in two different gneiss types. The main rock forming minerals in these gneiss types are quartz, feldspar, biotite (partially chloritized) and muscovite. Besides dumortierite, smaller amount of cordierite, tourmaline, andalusite, sillimanite, garnet, apatite and zircon also appear. We examined these rocks in thin sections with polarising and scanning electron microscope, too. A test with Raman-spectroscopy verified the identification of dumortierite and clinohumite. Afterwards, we searched for possible source regions, where the two studied special rock types occur close to each other. In Wachau, Austria these two rock types (Gföhl Gneiss and the marble of the Drosendorf Series) with key minerals (dumortierite and clinohumite) occur within few kilometres, in the vicinity of the recent (and former) bed of the River Danube. In the framework of a field trip, we collected rock samples from 22 outcrops. Two big quarries close to the Danube (Klein-Pöchlarn–Ebersdorf and Loja) seemed to be the most revealed and suitable locations. We correlated the collected samples (dumortierite bearing gneiss and clinohumite bearing marble) with those collected in Dunavarsány by the means of the upper mentioned methods and confirmed strong similarity between them.

With the knowledge of the place of the most possible origin, the fairly angular shape and the bigger size (gneiss: average 30 cm in diameter, marble: 80 cm in diameter) we suggest, that the most probable mean of transportation was the fluvio-glacial process. In this progress, the rocks fall, roll and/or solifluctate from the cliffs onto the river ice and raft even hundreds of kilometres along to the lower reach of the river. There the climate is appropriate for the ice floe to melt, so the rocks can fall down onto the river bed. These phenomena made possible for us to find unique rock types from the Austrian part of the Bohemian Massif in the middle of Hungary.

## Analysis of the impact of climate change on the formation of groundwater recharge

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This research is dedicated to the evaluation of the impact of climate changes on the formation of groundwater recharge.

Field experiments were conducted in the south-western part of the Moscow artesian basin (MAB), which is situated in the Kaluga Region in Russia.

The climate of the Kaluga Region is temperate continental. The average annual temperature in the region fluctuates between 3.5–4.0°C to the north and between 4.0–4.6°C to the south. Warm period (with positive mean daily temperature) lasts for 205 days on the northern and 220 days on the southern part of the region.

In terms of precipitation, the Kaluga Region can be classified as the zone of sufficient moistening. Precipitation is unevenly distributed in this region: it varies from 390 to 867 mm on the northern part and from 422 to 858 mm on the southern part.

Input information is the climatic data (precipitation, temperature and air humidity) for the period from 1961 to 2012, collected by six meteorological stations in the Kaluga Region (Fig. 1). Increase in minimum, maximum and average air temperatures is observed since 1989 (Fig. 2). Analysis of the data indicates that from the 1961–1988 time period to the 1989–2012 time period, the average air temperature has increased by 1.13°C, the minimum air temperature has increased by 1.15°C while the maximum air temperature has increased by 1.05°C. The precipitation has increased from 4.4 mm/year to 68.3 mm/year.

Two-block model was used in the modelling of water balance processes of the formation of infiltration recharge.

In the first block, processes of precipitation, formation and melting of snow cover, canopy interception, canopy transpiration, snow evaporation, slope wash generation and moisture absorption of soil with account of seasonal soil freezing are modelled (Grinevskii & Pozdnyakov, 2010).

The second block is implemented in program HYDRUS 1D (Šimunek *et al.*, 2005) and represents a model of nonstationary moisture transfer in the unsaturated zone with account of processes of soil evaporation, water uptake by plants and water supply to groundwater level, infiltration recharge (Grinevskii & Novoselova, 2010).

Modelling was conducted for common landscapes (open, i.e. agricultural and closed, i.e. wooded), for common types of soils and unsaturated zones (clayey loam and sands) and for different depths of groundwater level (10 m, 5 m, 3 m, 1 m) (Grinevskii & Pozdnyakov, 2010).

The data of the landscape model are calibrated based on the comparison of the modelled data with the snow cover thickness.

As a result, variations in groundwater recharge in different landscapes are quantitatively described. It was mentioned that the average annual sum of the infiltration recharge, which can reach more, than 20 mm/year, significantly depends on the type of the landscape. For instance, the largest change in recharge was noticed for the closed landscape with sandy soil, while the least change in

recharge was noticed for the open landscape with the same soil type.

Patterns of seasonal climate-change-induced variations (which in turn significantly depend on landscape) in infiltration recharge and patterns of other elements of water balance were also analysed.

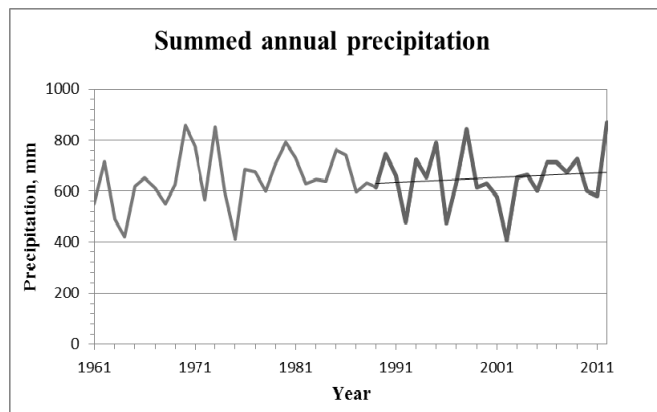


Fig. 1.: Graph showing annual precipitation sums for the period from 1961 to 2012 (trend line is drawn for the period from 1989 to 2012).

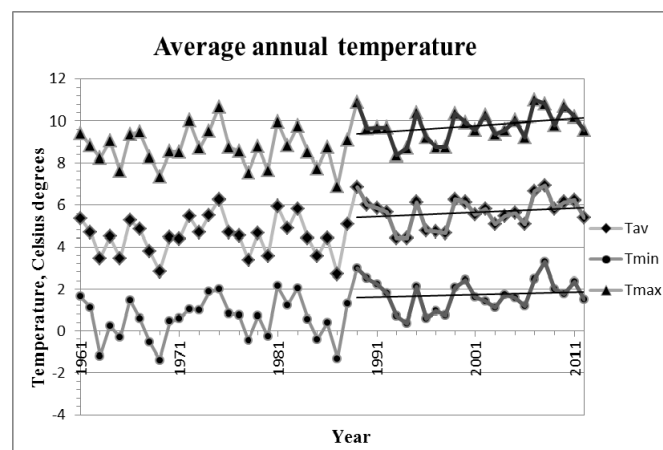


Fig. 2.: Graph showing average annual minimum (Tmin), maximum (Tmax) and average (Tav) temperatures for the period from 1961 to 2012 (trend lines are drawn for the period from 1989 to 2012).

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## Diversity of foraminifera in turbidite-interturbidite sequences from the selected deposits of the Siary Subunit, Magura Nappe (Polish Outer Carpathians)

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Fine-grained deposits of a turbidite sequence from the Magura Beds have been selected for detailed analysis. Pelitic intervals within 40 cm thick turbidite packet displayed vertical changes. Olive-green, calcareous layers, which showed the features of turbidites, were alternating with darker ones, which could be assumed as non-turbiditic, hemipelagic layers. The main aim of the study was to examine this sequence in terms of its foraminiferal content.

In 22 of the studied 24 samples, deep-water agglutinated foraminifers of flysh type (DWAF) were dominating. The number of specimens varied within the samples from 25 to 3569. The studied assemblages displayed low diversity, up to 16 genera. Most samples confirmed the assumption, mentioned by Winkler (1984) that in hemipelagic deposits foraminifers are more frequent, compared to their occurrence in turbidites. However, in a few cases, deviation from this pattern has been observed. This fact points to more complicated origin for the pelitic intervals of the turbiditic sequence, than it has been assumed from the macroscopic observations. In this case, statistic analysis could be a useful tool.

For both genetic types of pelitic sediments, the number of each genera was added up and two data samples, called A and B, have been created. As both data populations are not showing normal Gaussian distribution, only non-parametric methods were used. At first, the Mann-Whitney *U*-test was carried out. The standard, fundamental hypothesis of this test is that the two populations are identical. Data from both A and B sets were taken jointly and put in an ascending order. Each value had been given a rank on the basis of which *U* values were calculated and final results obtained as follows. Given hypothesis cannot be rejected with  $\alpha 0.10$  level of confidence. Under the assumption, that consecutive turbiditic currents came from same source area, the test result can be interpreted as there was no difference in the environmental conditions between the basin, from where currents originated and the basin of their deposition. It is also possible that foraminifer fauna was originally absent in transported sediments, but then was collected during the movement of the currents just before the deposition.

Another type of statistical method used in this study was the cluster analysis. It is a method of grouping data based on their similarity and presenting the results in a graphic form. R-mode clustering was used to discover, if there are any associations or patterns between the genera. In this approach, Euclidian distance was used as a measurement of taxonomic distance and then clusters were created by a single-linkage method. To present the findings, the cladogram style was chosen (Fig. 1.). *Dentalina* sp., *Psammospaera* sp. and *Hyperamina* sp. are very close, but their

number of specimen is very low and that could disturb the conclusions. The cluster layout confirms separation of the most frequent *Ammospheroidina* sp. and a tube-like taxa. Furthermore clustering showed, how distant occur from each other the rest of genera.

To do more advanced statistical analysis, more specific data is required. There are also more geological factors, which must be taken into consideration, in case if a more detailed environmental study based on statistical estimations is planned.

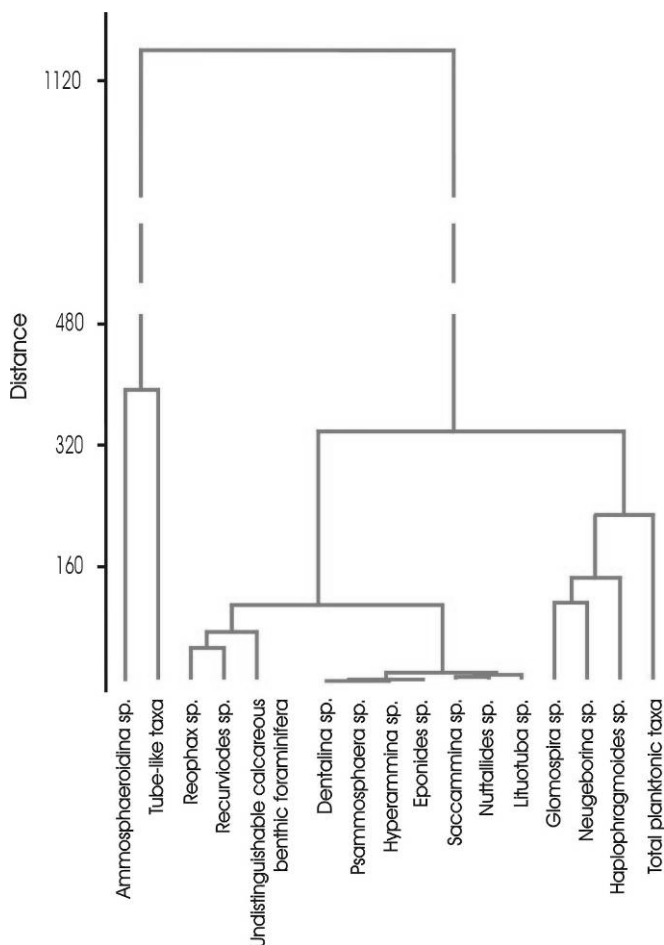


Fig. 1.: Relations between foraminifera fauna

Winkler, W. (1984): 2<sup>nd</sup> Int Symp Benthic Foraminifers: 611-617.

## Petrographic and geochemical investigation of the pyroclastics from Bondoró volcanic centre (western Pannonian Basin, Hungary)

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Bondoró is one of the youngest (~2.3 Ma) and most complex eruptive centres of the Bakony-Balaton Highland Volcanic Field (western Pannonian Basin, Hungary), that belongs to the post-extensional monogenetic alkaline basaltic volcanic fields in the Carpathian-Pannonian Region. The Bondoró volcanic centre consists of different eruptive units, each produced by different eruptive mechanisms: first, phreatomagmatic eruptions built up a tuff ring which was filled by basaltic lava afterwards. In the last phase, magmatic explosive eruptions (and related lava flows) occurred and a scoria cone was formed. This complex volcanic structure and the discordance observed in the succession suggest that Bondoró is a polycyclic monogenetic volcanic centre (Kereszturi *et al.*, 2010). Former studies of the lava rocks and basaltic bombs revealed that the Bondoró alkaline basaltic magma is unique among the Pannonian Basin basalts: it contains a vast amount of lithospheric mantle-derived xenocrysts (~30 vol%) and xenoliths (Jankovics *et al.*, 2013). This xenocryst enrichment caused the high concentration of refractory elements (13.1-13.9 wt% MgO, 459-490 ppm Cr, 444-570 ppm Ni), therefore the whole-rock composition of this basaltic rock does not represent the original magma composition.

My research focuses on the petrographic and geochemical analysis of the oldest products of the volcanic centre which is represented by the tuff ring sequences built up by tuffs, lapillituffs and lapillistones. Detailed petrographic investigations confirmed that the juvenile basalt fragments of these pyroclastic rocks also contain abundant xenocrysts and xenoliths, thus their whole-rock compositions are modified as well (similarly to the younger products of Bondoró).

To find out the original composition of the basaltic magma erupted to the surface, sideromelane glass shards of the pyroclastics were carefully analysed which represent the quenched, fractionated melt produced by the phreatomagmatic eruptions. Detailed investigation of these glass shards is often the only possible tool to reveal the parental magma composition in the case of basaltic pyroclastics. The glass shards were analysed based on their colour, crystal content and chemical composition. Four different crystal phases were observed: olivine (7.1-15.1 vol%), clinopyroxene (5.4-10.8 vol%), plagioclase (3.5-10.6 vol%) and Fe-Ti-oxides (1.5-2.5 vol%). The glass shards have phonotephritic and tephriphonolitic compositions (2.6-3.3 wt% MgO).

For the major element geochemical modelling, compositions of the olivine phenocrysts (Fo<sub>76-88</sub>) were measured in the studied glass shards, while in the case of the other crystals, previous mineral chemical data from the Bondoró lava rocks were used (Jankovics *et al.*, 2013). In the knowledge of the amount of the different phases, together with their compositions, mass balance calculations were carried out to approximate the major element composition of the parental magma. During this modelling procedure, it is required to assume a chemically closed system and homogeneous glass compositions. The calculated parental magma compositions are tephritic/basanitic and phonotephritic (6.5-9.5 wt% MgO). The measured glass compositions and the calculated compositions fit in the alkaline fractionation trend.

Using sideromelane glass shards for major element geochemical modelling in monogenetic volcanic centres is a useful tool to reveal the composition of the parental magma, when the whole-rock composition (the usual approach) is not adequate. The Bondoró alkaline basalt is a good example for this, because of the significant contamination by the xenocrysts. This geochemical modelling can also be applied in the case of such monogenetic eruptive centres, where no suitable lava rocks or juvenile basalt fragments of pyroclastics are available.

Recent studies suggested that polycyclic monogenetic centres (e.g., Udo, Jeju Island, South Korea; Brenna *et al.*, 2010) can be supplied by compositionally different magma batches, thus it is essential to carefully investigate every eruptive unit of a volcanic centre. However, this can be problematic in pyroclastic strata, which contain scarce amount of juvenile basalt fragments. Through the investigation of sideromelane glass shards of the pyroclastics and whole-rock geochemistry of lavas/bombs, it is possible to approximate the parental magma compositions in the different eruptive units of a volcanic centre, enabling us to identify any compositional differences between the erupted magma batches.

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Jankovics, M. É., Dobosi, G., Embey-Isztin, A., Kiss, B., Sági, T., Harangi, Sz., Ntaflos, T. (2013): *Bull Volc*, 75/9: 1-23.  
Kereszturi, G., Csillag, G., Németh, K., Sebe, K., Balogh, K., Jäger, V. (2010): *Centr Eur J Geosci*, 2/3: 362–384.

## Contact mineral phenomenon on the example of Pobuzhskiy granulite complex (Ukrainian Shield)

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The schists of the Salkivska suit from the Pobuzhskiy Granulite Complex (Ukrainian Shield) were investigated in this work. Their approximate modal composition according to optical microscopy data is the following: amphibole 40 vol%, plagioclase 35 vol%, orthopyroxene 15 vol%, clinopyroxene 10 vol% (Fig.1).

Scanning electron microscopy and microprobe (EDS) analysis were carried out at the Geological Faculty of the Kyiv National University of Taras Shevchenko. The used accelerating voltage was 20kV, the element detection limits were between 0.01-0.1 wt%, the error measurement accuracy was 2-10 rel%, while the spatial resolution was 5-10  $\mu\text{m}$ .

The research was done on the mineral boundaries of orthopyroxene and clinopyroxene along a profile (Fig.2).

The results of studying the orthopyroxene/clinopyroxene boundary demonstrate zonality of the composition of these minerals (Fig. 3.). We assumed, that this zonality has caused by amalgamation of mating flanks of orthopyroxene and clinopyroxene (OPx-CPx). Weight parts of each phase within each zone have been estimated using the following formula:

$$a_1 = \frac{Ca_{1-2} - Ca_2}{Ca_1 - Ca_2},$$

where,  $Ca_{1-2}$  is the measured content of CaO on the “shelve”;  $Ca_1$  and  $Ca_2$  are the evaluated contents of CaO in orthopyroxene and clinopyroxene, respectively. The contribution of the OPx and the CPx on the “shelve” was estimated using the following formula:

$$C_1^* = C_1 \times a_1; C_2^* = C_1 - C_1^*$$

where,  $C_1$  is the wt% of oxides in the OPx.

The efficiency of the accepted model is confirmed by the coincident of the measured and the evaluated values of oxides in the orthopyroxene and the clinopyroxene (Fig. 4.).

Calculation of the formation temperature of the current mineral association has been made by the program QUILF. Input data were proportions of minerals X(En) and X(Wo). We made estimates in different ways: 1) using minerals of OPx and CPx from the peripheral parts; 2) using minerals of OPx and CPx from the inner zones; 3) using minerals of OPx and CPx, that have been calculated above.

In the first case, we got a temperature about 650°C, in the second case, 1500°C was calculated, while in the third case, a formation temperature of 620°C was got.

The similarity between the first and third cases has evidenced the reality of the accepted model about the paragenesis of the examined minerals.

However, the fact of the presence of such “shelves” requires additional research.

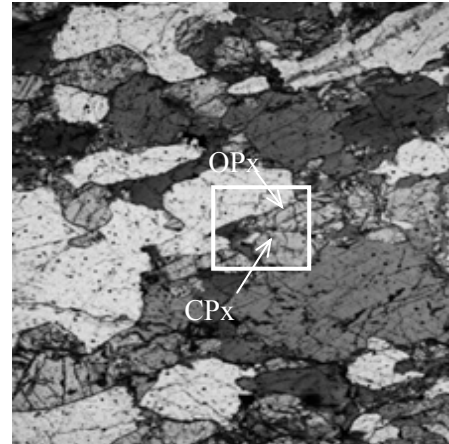


Fig. 1.: Image of t amphibole-plagioclase-two pyroxenes schist in thin section (PP).

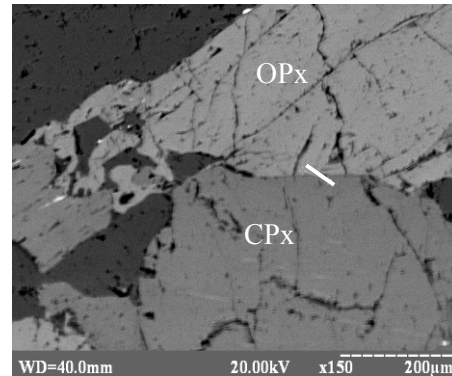


Fig. 2.: Microprobe image (BSI) of the investigated area. The analysed profile (see Fig. 3.) is shown with a white line.

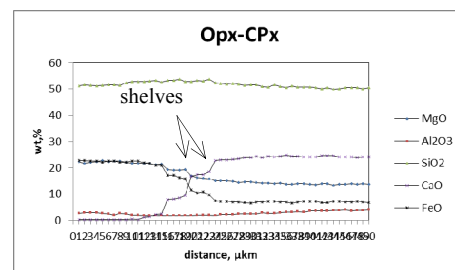


Fig. 3.: Composition of the OPx (left part) and the CPx (right part)

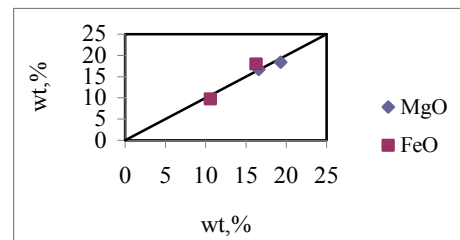


Fig. 4.: Comparison of the measured (x) and the evaluated (y) contents of the oxides in orthopyroxene and clinopyroxene

## Oil outcrops in the Croatian part of Pannonian Basin System as a field trip research object of Petroleum Geology course

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This work comprises data about oil outcrops in the Croatian part of the Pannonian Basin System (CPBS) based on field trip research of a Petroleum Geology course. Field trips are held to conclude, in which geological circumstances can be seen outcrops of reservoir rocks and oil on surface. The Pannonian Basin System is a back-arc-basin system, where in the past the Central Paratethys was located, and after it, brackish and fresh-water environments formed (Velić *et al.*, 2012). Basins, depressions and subdepressions were formed along dextral and sinistral strike-slip faults. CPBS belongs to its southwestern part and it is divided into the Drava, Sava, Mura, and Slavonija-Srijem depressions. The general depositional environment is very similar in all parts of the basin. It is divided into three megacycles, mainly infilled with Neogene–Quaternary rocks.

From NW to SE, there are three main sites, where oil outcrops are found (Fig. 1.). Peklenica, located in the Medimurje region, belongs to the Mura depression. Oil outcrops (visible irisation) can be seen in the Peklenica Stream and around an old mining shaft. Outcrops correlate with the Selnica–Peklenica anticline (Velić, 2007).



Fig. 1.: Topographic map showing the locations of the outcrops.

To the southeast, there is another location in the Sava depression, called Mikleuška (Fig. 1.), named after a village 2 km away. In Mikleuška, traces of oil tar and bitumen from bituminous schists were found but it was not enough for profitable exploitation. The next significant place on that territory is a 72 m deep well „Martin“, which intersects granitic rocks saturated with oil. At the bottom of the shaft, nine horizontal halls are found, which are following fractures in the granitic host rocks. Oil was situated in the fractures of granitic rocks and in the upper sedimentary rocks. It is brown to black coloured, hardly flammable and burns with fuliginous flame. Approximately a few hundred litres of oil were put in barrels and uplifted to the surface daily (Žgaljić, 1984), with a total of 100 t annually from 1854/1855 until 1943 (Gretić & Bobić, 2002). Clays on the top stops oil to lift up to the surface, so the only natural outcrops are those ones, where oil seeps out from sides of the stream. Surrounding area consists of Paleozoic and Mesozoic magmatic and metamorphic with Neogene sedimentary rocks. From lithological

point of view, the surrounding rocks are Miocene sandstones and marls and Pliocene beds. The outcrops are not on the surface because they are covered with Quaternary sediments.

The southernmost location is the village of Paklenica (Fig. 1.), located 100 km SE from Zagreb. It also belongs to Sava depression. Oil is noticed in the Paklenica Stream, mostly in the upper part. Oil outcrops are also found in the bottom of Sisvete Peak (321 m) and in the valley of the Voćarica Stream. CH<sub>4</sub> and H<sub>2</sub>S gases are also present. There are a few shallow shafts along the anticline Kozarica. Going through the valley of the Paklenica Stream, crossing over the structure called structural nose, there are outcrops starting from Pleistocene sediments represented by gravel and sand. Pleistocene sediments are followed with Pliocene beds (clay and sand), with an occasional appearance of lignite. In upper Miocene beds (Pontian) coal has been found and excavated along a 50-m-long pit. Lower Pontian beds are the host rocks for some hydrocarbons. Pannonian beds consist of white marls, while Sarmatian is represented by laminated marls that are mostly bituminous. Those marls are the source rocks. The structural nose in its middle part has *Lithothamnium* limestone and Badenian sandstone. In the upper part, bituminous marl is found. The top of the structure is eroded. Thus, without an adequate seal, oil outcrops are found on the surface.

We have come to the conclusion, that oil outcrops in Peklenica and Mikleuška are similar. The sides of the streams are eroded, so the horizontally flowing oil is going out from the source rocks and seeps slowly, but continuously into the streams. Other recent occurrences are in the old mining shafts, where oil is mixed with water now. However, the situation in Paklenica is different. There is an uplifted structural nose, which is uncovered, so oil appears on the surface from abandoned wells.

The names of those villages Paklenica, Peklenica are significant, and may have the same origin from old Croatian words „*pekel*, „*paka*“ which means oil tar. Today these outcrops are just of historical significance, interesting, because oil is still on surface. On the other hand their present day economic value is negligible.

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## **The results of sedimentological and gamma-ray logging of Upper Miocene lacustrine turbidites of the Transylvanian Basin**

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The Miocene sediments of the Transylvanian Basin are important reservoirs of natural gas production. Recent studies have focused on the sedimentology and the palaeoenvironmental reconstruction of Upper Miocene sediments, but an in-depth study is lacking from the south-western part of the basin. Thus, our aim was to examine the less studied lacustrine turbidite outcrops in detail and set up an environmental reconstruction. In addition, we measured gamma-ray logs to investigate the relationship between facies and gamma-ray response. Studies at the scale of geophysical logs and outcrops together provide a curious perspective on reservoir characterization.

Detailed facies analysis was carried out in six outcrops. In four of them, the natural gamma radiation of the sediments was measured in a vertical log with a handheld 1024-channel gamma-ray spectrometer. A corresponding sedimentological log was drawn in

the same vertical section. To find the appropriate measuring time and resolution, first several test measurements were done in the field: 60 sec/point and 10 to 3 points/metre gave the optimal result.

We have found the products of different sediment gravity flows: high density gravelly and sandy as well as low density turbidity currents and sandy debris flows alternated with settling of mud. Architectural elements of deep-water fans: complex channel fills, channel-levee systems and lobes were identified. The development of the systems in outcrop scale was also investigated. The measured gamma-ray logs do characterize the architectural elements. The observed complex channel fills, the channel fill part of channel-levee systems and lobes are all good reservoir analogues even though their geometry, volume, internal heterogeneity and connectivity differ.

## The importance of electromagnetic methods to build numerical groundwater flow model for an area with complex geology in the case of Tihany Peninsula, Hungary

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Wetlands and the understanding of their connection with groundwater is a highlighted topic nowadays. These areas have an important role in maintaining the biodiversity of earth, therefore they require protection. Groundwater influenced lakes and wetlands are hydrologically and ecologically linked to adjacent groundwater bodies, but the rate of their interactions is highly variable. A lake can gain groundwater or lose water to the groundwater systems and these processes can vary in space, depending on the position of lake in flow systems, moreover in temporally. The lakes can connect to the groundwater in three different ways: recharge, discharge type, and flow-through lakes (Winter *et al.*, 1998). This relationship depends on the water table configuration, relation of the lake water level to the water table and to the subsurface potential field, the geological framework, climate, and the vegetation around the lake (Winter 1976, 1978).

These issues are more complex in areas with complex geological settings. The understanding of groundwater flow systems here therefore have high importance in water supply issues, land use planning or in management of natural conservation areas. The study concentrates on the Tihany Peninsula (natural conservation zone) surrounded by the Lake Balaton, Hungary. The lakes of the peninsula are located in paleo-maar structures being formed during the Neogene phreatomagmatic volcanism of the region (Németh *et al.*, 2001). The lakes were supposed to be recharged exclusively from precipitation. However, based on the above mentioned considerations, and on the numerical and theoretical studies of Winter (1976), connection of the lakes with the groundwater can be presumed. In this area, beside the primary effect of the topography, the geology significantly controls the flow systems: the paleo-maar environment, the variation of siliciclastic and carbonate rock formations, and the tectonic features. The main goals of the study were (1) to understand the groundwater flow pattern in that complex geological framework, (2) to determine the hydraulic position of the lakes in the flow systems of the Peninsula and to find explanation for the different hydrological behaviour of the lakes and (3) to evaluate the connection of the groundwater system with Lake Balaton.

The hydraulic data for the whole peninsula are scarce; therefore 3D numerical modelling (Comsol Multiphysics 4.2a) was used to achieve the purposes. In order to build up a model, hydrostratigraphic characterization of the geological formations was achieved. Indirect geophysical methods were used to determine the geometry of the units and the hydraulic conductivity: radio-magnetotelluric (RMT), audio-magnetotelluric (AMT), VLF resistivity, VLF electromagnetics and gradient methods. Hydraulic conductivities were derived by conversion of the measured resistivity values. Based on the detailed geological characterization, the flow systems were simulated during different scenarios.

As a result of the study (1) a hydraulically continuous subsurface flow field was recognised for the area, which is driven mainly by topographic gradients. The model (2) indicated the different hydraulic position of the lakes, in good agreement with the field measurements (hydrogeochemical analyses, ecohydrological, archive and recent field observations): the Ráta Csáva, situated in the highest topographic position, is a recharge lake. The Inner Lake can receive water from the surrounding local heights and it can lose water toward the Outer Lake. The Outer Lake is in the lowest topographic position consequently it is a discharge lake receiving groundwater from every direction. Furthermore, the study revealed: (3) hierarchically nested flow systems for the whole succession, (4) the barrier role of Pannonian Formations in flow field and the hydraulic behaviour of structures, (5) the diffuse discharge at the edge of the peninsula, (6) groundwater discharge in the Lake Balaton in ~50 m wide zone around the peninsula (Fig. 1).

These conclusions can be decisive concerning water balance and ecological aspects of these wetlands as well as in the management of the nature protection area. The results can also initiate further research to understand the interaction between flow systems and lakes in similar geological environments.

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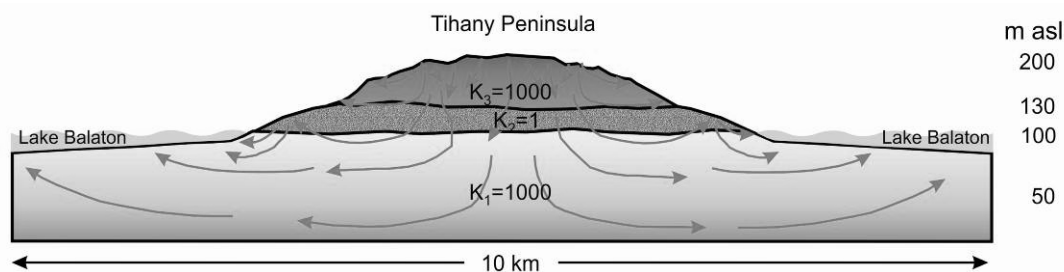


Fig. 1.: Schematic figure of the flow system of Tihany Peninsula. This pattern can be generalized for geologically complex peninsula

## Overpressure Occurrence and Mechanism in Blora-Tuban Region, East Java Basin, Indonesia

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The East Java Basin is well known as an overpressured basin in Indonesia (Kamaluddin *et al.*, 2011). The manifestation of the overpressure, i.e. mud volcano is ubiquitous in this basin (Satyana & Asnidar, 2008). This paper discusses results from the western part of the East Java Basin, from Blora and Tuban regions (Fig. 1.). The methods used in this study are drilling parameter and wireline log analyses with additional data from scanning electron microscopy (SEM).

The mudweight used while drilling in a typical well in the area is shown on Fig. 2. The mudweight starts to increase significantly at the depth around 1100 m, corresponding to the deflection in d'exponent (Fig. 2., right). Based on this observation, it is implied that the top of the overpressure is located at the depth ~1220 m. Lithologic column (Fig. 2., left) shows that starting from the depth ~1000 m, sand content starts to decrease significantly. In this well, sloughing shale is associated with connection gas, thus drilling pipe stuck at depths 1100 – 3000 m. This is caused by the presence of high overpressure as indicated by significant increase in mud weight. Density, sonic and resistivity data in the shale section reverse toward the low density and resistivity and high neutron porosity and sonic velocity, at depth ~1250 m (Fig. 3.). This depth corresponds to the increase in mudweight and deflection in d'exponent (Fig. 2.). Therefore, overpressure in this well is responded fairly well by neutron porosity, density, sonic and resistivity logs.

In order to analyse the cause of overpressure, a cross-plot between density and sonic data is constructed. Starting from the surface, down to the depth of 1250 m, the shale points are located in a smectitic line. Starting from the depth of 1250 m (top of overpressure), down to the depth of 2100 m, the data are located in the transition between smectitic and illitic line. These circumstances indicate that there is strong relationship between the presence of overpressure and smectite to illite transformation. From the depth of 2100 m to 3000 m (TD), the data are located in the illitic line, corresponding to the presence of higher overpressure (Fig. 4.).

The presence of authigenic clay minerals, i. e. smectite-illite, illite, kaolinite and chlorite detected from SEM analysis (Lemigas, 1989) confirms that diagenetic clay mineral occurs at the depth of 1100–3000 m (TD). Based on the above analysis, it can be concluded that in the study area, overpressure could be observed from drilling parameters and wireline logs. Furthermore, the analyses of wireline logs and clay mineralogy show that the smectite to illite transformation may contribute to the observed overpressure in the studied area.

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Authors thank to INOV (Indonesia Overpressure Study) ITB and Pertamina E&P for the opportunity to study overpressure in The East Java Basin.

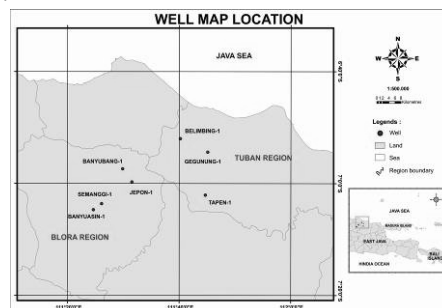


Fig. 1.: Map of research area

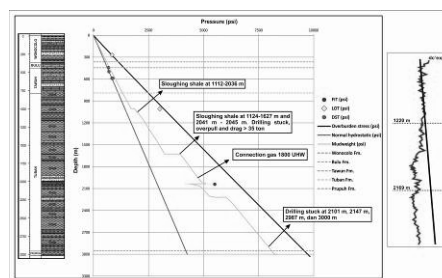


Fig. 2.: De'exponential in a typical well (Banyubang) shows deflection from normal trend at 1220 m (Pertamina, 1989) and drilling parameters also show indication off overpressure

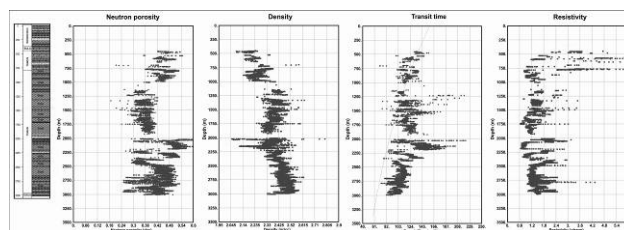


Fig. 3.: Wireline logs response in shale lithology (left to right: neutron porosity, density, sonic and resistivity logs) in a typical well (Banyubang) show deflection from normal trend in 1250 m that indicate an overpressure

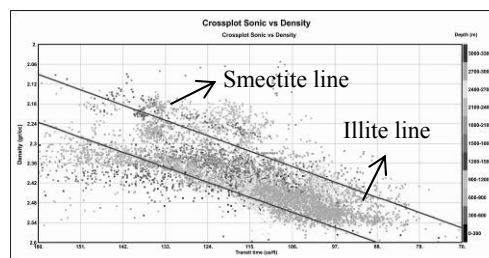


Fig. 4.: Crossplot density (Y) vs. sonic log (X) in shale lithology at a typical well (Banyubang) show movement of data from smectite line to the illite line starting at 1250 m.

## Deformation stages in granitoids of uranium deposit: reconstruction on the basis of special technique of microstructural analysis

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Cracks in rocks can be considered as Open Cracks (OC: not filled with secondary mineral phases) or Filled Cracks (FC: filled with secondary mineral phases or fluid inclusions). FC are often partially filled or reopened after a first event of filling. The best records of fluid percolation are paleofluids trapped as Fluid Inclusions (FI) in healed microcracks of the rock-forming minerals (Lespinasse *et al.*, 2005). Usually such FIs with liquid, vapour and solid phases form differently oriented systems, known as Fluid Inclusion Planes (FIPs). FIPs are result from the healing of former open cracks and appear to be fossilized fluid pathways (Roedder, 1984). FIPs are totally sealed and do not present secondary opening.

Microcracks should provide valuable information about the local stress and deformation in rocks and can be assumed to be ( $\sigma_1\sigma_2$ ) planes (Tuttle, 1949). The FIPs are mode I cracks that occur in sets with a predominant orientation perpendicular to the least principal compressive stress axis  $\sigma_3$ . These mode I cracks propagate in the direction which favors the maximum decrease in the total energy of the system. They do not disrupt the mechanical continuity of mineral grains and do not exhibit evidence of shear displacement like mode II and III cracks. The FIPs are usually observed and characterized in minerals which crack according to the regional stress field, independently of their crystallographic properties, and may easily trap fluids as fluid inclusions when healing. The rate of healing is most rapid in quartz (compared to geological times), so it is more informative for studying FIPs systems (Lespinasse, 1999).

FIPs form well defined networks. This fact allows revealing a chronology of different deformation stages of rocks. When a first generation of FIPs formed, a second crack family can be formed, cross-cutting the first one. Thus, FIPs provide good records of successive episodes of crack initiation and fluid migration.

As orientation of FIPs is defined by reorganization of the local stress field so besides reconstruction of deformation stages it is possible to use them as geostructural markers for reconstruction of porosity and paleopermeability of rocks, geometry of fluids migration pathways, reconstruction of fluid migration stages and for studying dynamics of change of PT, physical and chemical conditions at various events of deformation of geological objects.

FIP generations were studied at the giant Antei uranium deposit. Besides there were studied different types of microcracks – filled with mineral phases, partially filled, filled with ore components, opened and reopened cracks (Ustinov & Petrov, 2012). Antei uranium deposit is located in Eastern Transbaikalia within the Streltsovskaya caldera, generated in process of late-Mesozoic activation of tectono-thermal processes in the region. Samples were taken from main fault zones – from the central part (core), the zone of its dynamic effect (failure), and undestroyed wall rock (protolith) at the 9<sup>th</sup> and 11<sup>th</sup> horizons. Microcracks of different types were studied by means of special technique of microstructural analysis. For realization of this technique it is important to take samples oriented in space. The considered method allows to carry out

statistical analysis of 2D digital images of thin sections by means of the special software and thereby to reconstruct chronology of deformations. Besides, this analysis allows quantifying paleofluid flow porosity and permeability by the reconstruction of the crack network consisting of cracks described as discs using the geometry of the crack network. Using microstructural analysis one can determine dip direction, length, thickness, porosity and paleopermeability for each microcrack system. The data on composition and properties of fluid inclusions trapped by cracks (temperature, pressure, salinity and phase composition) to separate different sets of FIPs can be found out using microthermometry and Raman spectroscopy.

As the main ore component of the Antei deposit is uranium, also it was used sufficiently effective method for reconstruction fluid filtration processes and stages of intraore tectonics during the past geological events – fission-track radiography (FTR) of thin sections.

The comparative characteristic of orientation of different types of microcracks and objects was carried out by construction of roses-diagrams for each type of objects. It allowed defining spatial parameters of chosen linear objects and allocating stages of deformation and fluid migration, to confirm conception about polystage development of the intraore tectonic processes.

After getting spatial parameters of each microcrack generation, FIP system, making their interpretation and finding out distribution of uranium ore the following conclusions can be drawn:

1) Hydrothermal process at the Antei uranium deposit took place through four main stages of deformation with differently oriented microcracks which trapped fluid inclusions with different properties. Each stage of deformation directly connected with certain events of transformation of ore containing rocks.

2) According to the FTR and microstructural data the intraore tectonic processes occurred during two main stages of uranium-bearing fluids inflow.

3) This approach can help us to model porosity and paleopermeability of crystalline massifs (tectonics, fluid flow pathways, fluid chemical composition, etc.) as a function of stressed-strained and temperature state in space-time context.

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## The hydrodynamic entrapment model of the Tatárülés-Kunmadaras gas field

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In my work I examined the entrapment conditions of the Tatárülés-Kunmadaras gas field, which is related to a basement protrusion near Berekfürdő, East-Hungary. Hydrogeological interpretation has already been done for this area, for which I made oil hydrogeological investigations. The gas field was discovered and set production near Kunmadaras in the 1950s. My purpose was to explain the location of the field with oil hydrogeological investigations and on this basis, substantiate the effectiveness of the method.

In my work I used the “UVZ” method. This uses the basic principles and equations which were described by Hubbert (1953). The method wants to determine, in what amounts the hydrocarbons can accumulate and preserve in various geological and hydrogeological conditions. This procedure examines the hydrocarbon migration on hydrodynamic basis, emphasizing the role of water flow. The basic theory of the method is that the hydrocarbons move along with water, however their flow directions differ due to the density difference. The basic equation is:

$$U = V - Z,$$

in which  $Z$  is the elevation,  $V$  is the water potential with respect to oil or gas and  $U$  is the oil or gas potential. The method is basically graphic, the  $Z$  contours are the isolines of the reservoir top map. The  $V$  contours are the rescaled versions of the water equipotentials based on density differences. With the help of the  $V$  and  $Z$  contours, we can map the  $U$  potential surfaces. The three variables represent the combined effects of the lithological changes, the trap structure and the hydrogeological environment (Dahlberg, 1995). During the procedure we are looking for areas, where the potentials of the analysed fluids reduce to a minimum, because every hydrocarbon particle will migrate towards these zones. It is necessary for the minimum contours to be closed, so the fluid particles cannot release. In terms of hydrocarbon entrapment, the best occurrence is when a closing potential minimum overlaps with an anticlinal structure, but single minimum areas can hold large amounts of hydrocarbons, too.

To test the “UVZ” procedure, I have chosen the Tatárülés-Kunmadaras gas field, because there the structural and hydrogeological factors influence the entrapment of the hydrocarbons. The hydrocarbons stored in two main Pannonian reservoir layers. There are three principal fault zones in the area, which delineate the gas field from East and West (Czauner & Mádl-Szőnyi, 2011). Along these fault zones, the upwelling of water is very strong. The convergence of these fault zones marks the southern border of the field.

During my work I had only data from the upper reservoir strata. I made water equipotential maps, water potential maps with respect to gas, gas potential maps, hydraulic cross sections, water potential cross sections with respect to gas and gas potential cross sections. I

made the calculations with three different gas density values, because I did not have an accurate value.

Based on my results, between the three fault zones in the examined reservoir, the direction of the water flow is west to east, which affects the gas entrapment. Consequently, the upwelling along the western fault is stronger, than along the eastern one. Based on the gas potential maps and cross sections, I showed that the gas entrapment is hydrodynamically possible in the area. The closed potential minimum zones are visible in every gas potential map and cross section. The most favourable area for the accumulation of gas is in the eastern side of the area, where a closed gas potential minimum overlaps with an anticlinal structure.

The sections also show the impact of hydrodynamic environment on the hydrocarbon accumulations (Fig. 1.). This manifest in, that at the case of the western, bigger anticlinal structure the minimum values of the gas potentials, so the most probable places of the accumulation of gas are not located in the hinge zone of the structure, but these are in tilted position to southeast.

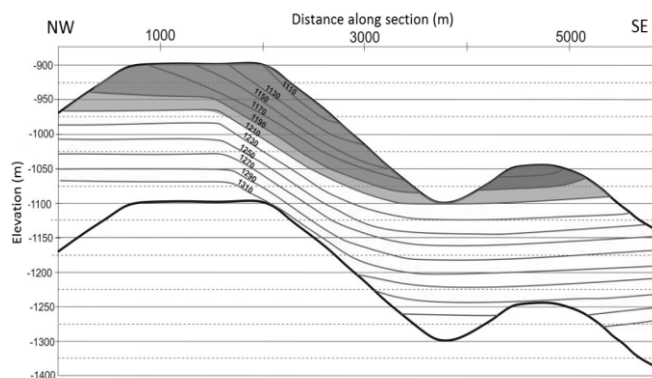


Fig. 1.: The gas potential section made with density value  $0.4 \text{ g/cm}^3$

It also proves that the gas field, what was discovered here in 1957, can be bigger. Some of the hydrocarbons could have washed towards east, southeast directions before the production. Based on this, the re-accumulation of hydrocarbons was possible in this directions.

Based on my results the Tatárülés-Kunmadaras gas field accumulated in a hydrodynamic trap. In this case, the “UVZ” method was suitable for the more accurate delineation of the trapping sites, so it can be an effective method in other fields, too.

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## The geochemical argumentation of the geodynamic control scheme of the Neogene volcanism in the Ukrainian Carpathians

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The volcanic centers of the Transcarpathian region groups in two lines: the south-western Chop line and the north-eastern Vygorlat-Huta ridge. The location of the effusive rocks in the central and western part of the Vygorlat-Huta ridge is controlled by the tectonic evolution of the Transcarpathian deep fault. The Poprichyi, Antalovskiy, Syniak and Boryliv Dil volcanic tracts are characterized with andesite-basalt—andesite—andesite-dacite—dacite—liparite-dacite compositions. The Velykyi Sholes tract is composed of andesite-basalt—andesite—dacite—liparite volcanic rocks. The formation of this tract is closely associated with a submeridional fault that formed on the border of the Chopska and the Solotvynska depressions (Merich & Spitkovskaja, 1974).

Tolstoi *et al.* (1976) have considered that Pliocene volcanic rocks of the Vygorlat-Huta ridge formed in a petrochemically consecutive line. That fact can be interpreted as an evidence of their common formation. But, in spite of the common petrographical and chemical characteristics of Vygorlat-Huta volcanic rocks, there is some lateral differentiation in their composition:

- the compositions of the volcanic rocks of Oash and Velykyi Sholes are more alkaline than the compositions of volcanic rocks of Poprichyi, Antalovskiy and Syniak tracts, that are related to the Transcarpathian deep fault;

- basalts and andesite-basalts of Oash and Velykyi Sholes volcanic tracts are characterized with enriched Na<sub>2</sub>O and slightly depleted MgO content;

- in all kinds of plagioclases, the Ab-component is higher in Oash and Velykyi Sholes volcanic rocks than in rocks of Poprichyi and Syniak tracts;

- the volcanic rocks of Oash and Velykyi Sholes tracts are more ferruginous, than the other volcanic rocks of the Vygorlat-Huta ridge;

- the Ti/Mn proportion, that is considered as the depth indicator of volcanic rocks formation (Abramovich & Vysokoostrovskaja, 1964), rises from 3.0-4.5 in Syniak volcanic tract to 10.5 in Oash and Velykyi Sholes volcanic tracts.

These features of the different parts of the Vygorlat-Huta ridge demonstrate the relation between the chemical composition of igneous rocks and their relation to the definite faults on research area. These geochemical data with preliminary structural-paragenetic

analysis of the Transcarpathian faults grid, as well as magmatic center distribution data, permit to suggest a new dynamo-kinematical scheme for the Neogene volcanism in the Ukrainian Carpathians.

According to this scheme, the general submeridional compression process of the Carpathian fold system caused the right-side split zone in Transcarpathia.

The split zone is restricted on the north by the Transcarpathian deep fault, which is characterized by a north-western strike and a subvertical decline. The southern boundary is not that clear. It includes the territory between the Samozh (Somezh) fault and the Pannonian deep fault, where dislocation movements were complicated, probably, by shifting of the tectonic blocks. The split zone, stated above, is joined by the "S"-like Vygorlat-Huta volcanic ridge. The central section of Vygorlat-Huta is oriented with an angle of 50° to the Transcarpathian deep fault zone. The Preshiv volcanic ridge has almost the same orientation.

The split zone and the active magmatic structures of dilatation form the flaw structural paragenesis, which is complicated by faults of higher degree (synthetic R- splits and antithetic R'-splits). On some geological maps, faults with ancillary P-splits can be also found. Intensification of noncoaxial movements in the split zone activates the turning of the break structures (which causes their extension) and Riedel splits.

The suggested geodynamic control scheme of Neogene volcanism in the Ukrainian Carpathians offers a perspective both in theoretical and research prospects with further substantiation of this scheme.

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## Water quality of the upper flow of the river Kolubara

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The problem of pollution of water resources and surface and underground waters is always a popular subject. Surface streams, which flow through populated areas and industrial zones, unfortunately represent a recipient for polluted waters that in most of the cases go to the stream without any filtering and control. The city of Valjevo (90 000 inhabitants) is located in West Serbia, in the upper part of the basin of River Kolubara. The most important industrial zone in Valjevo is, qualified as a metal and agricultural-food complex, but textile industry, furniture industry, printing press and metal processing are also presented there. The city was developed on the upper part of the River Kolubara. The river represents a recipient for all industrial and municipal polluted waters.

The Hydrometeorological Institute of the Republic has an observation network on the upper part of River Kolubara, as well as on its tributaries Obnica, Jablanica, Gradac. However, the quality control of the water is not fully covered by the observation network.

The last research about the water quality of River Kolubara have been done in 2004 (Santrač & Daskijevic, 2004) and they have shown that River Kolubara belongs to the last, 4<sup>th</sup> class of watercourses according to its quality. That means that water is not usable without some previous treatment.

Here the results of the water quality research done in 2012 are presented. For this research we have chosen 8 places, from which 3 are located on tributaries (Obnica (1), Jablanica (2), Gradac (6)) and 5 are on Kolubara directly (Fig. 1.). The following water quality parameters were determined:  $\text{NH}_4$ ,  $\text{NO}_2$ ,  $\text{NO}_3$ ,  $\text{PO}_4$  content and content of organic substances that was represented by  $\text{KMnO}_4$ .

During the research, we found that the amount of some pollutants has been reduced, compared to the conditions documented in 2004. Due to a financial crisis, the biggest part of the industry has been extinct. The other small part still works, but with reduced capacity. A change of water quality has also been observed after inflow of polluted water from a brewery (2), mill (4), market (7) and collector for polluted waters (8) (numbers refer to Fig. 1.). Chemical analyses have shown significantly less concentrations of the examined polluting components, compared to the conditions of 2004. According to these parameters, the River Kolubara is classified to

3<sup>rd</sup> class of watercourses and it is possible to use for industrial necessities without previous treatment. The only parameter that goes above the maximal allowed concentration for this type of watercourses is the presence of organic substances on a sample that was taken right after outflow of polluted waters.



Fig. 1.: The city of Valjevo and River Kolubara, with the sampling points marked with white numbers.

Considering the fact that Kolubara originates from two rivers, which have basins linked to karst areas southwards from Valjevo and that its tributary Gradac has been declared as one of the cleanest rivers in Europe, it is obvious that Kolubara has a huge potential in its upper stream. To improve its quality, the best possible way would be to work actively on the legal regulations concerning the quality of polluted waters that go from industrial facilities to recipient rivers. Also it is very important to remove all illegal landfills that are located near the stream in the centre of the town.

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## Secondary zircon-group minerals originating by recrystallization of Sc,Y,U,P-rich zircon and complex W-Nb-Fe-Sc oxide from the pegmatite No. 3, Dolní Bory, Czech Republic.

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Zircon-group minerals are very important as indicators of geochemical fractionation, for age determinations, thermometry (zircon saturation thermometry, Ti in zircon) and they are considered as potential matrices for high level nuclear waste storage. Dolní Bory pegmatites provide excellent natural laboratory for investigation of their properties, such as compositional variability and behavior during recrystallization.

Pegmatite No. 3, about 5 m thick and several tens of meters long dyke, belongs to large population of NNW-SSE trending dykes, cross-cutting granulites of the Gföhl unit of the Moldanubian zone, Bohemian Massif. The pegmatite consists from contact inwards of: 1) granitic zone (microcline + quartz + oligoclase + biotite ± muscovite), 2) graphic zone (microcline + quartz), 3) blocky microcline, 4) quartz core, 5) albitic unit (albite + andalusite + schorl + sekaninaite) and 6) andalusite-diaspore nodule.

Both investigated mineral assemblages occur in about meter-sized andalusite-diaspore nodule enclosed in quartz core. Novák *et al.* (2008) determined the p-T conditions of crystallization of primary diaspore and andalusite at 400°C and 2 kbar. The nodule also contains younger pyrophyllite and kaolinite partially replacing andalusite and accessory schorl-foitite, ferberite-wolframoixiolite, rutile, ilmenite, monazite-(Ce), xenotime-(Y), zircon, autunite and pyrite.

Zircon rich in Sc, Y, U, P initially formed in association with monazite-(Ce), xenotime-(Y) and ilmenite. Subsequent hydrothermal alteration left the xenotime intact, partially replaced the monazite to REE-rich crandallite and caused complete recrystallization of the zircon (Fig. 1). Contrary to nearby located dyke No. 4, (Výravský & Novák, 2013) no primary zircon domains were found. Recrystallised zircon contains in average 9.7 mol% of pretulite ( $\text{ScPO}_4$ ) component, 0.7 mol% of xenotime component, 0.003 apfu U and Zr/Hf 35. The recrystallised zircon hosts numerous tiny pores, inclusions of secondary xenotime (0.021 apfu Sc, 0.036 apfu U, 0.006 apfu Zr) and inclusions of secondary pretulite (0.05 apfu Zr, 0.018 apfu Y, 0.0004 apfu U) all  $\approx 10 \mu\text{m}$ . Absence of uraninite inclusions in recrystallised zircon, which were found in similar zircon in dyke No. 4 (Výravský & Novák, 2013) indicates that excess of the released U, which did not fit to structures of forming secondary zircon-group minerals, was leached out by oxidizing fluids in the form of  $\text{U}^{6+}$  and precipitated away as common autunite.

Complex W-Nb-Fe-Sc oxide, ranging in composition from wolframoixiolite to ferberite ( $\leq 4.36 \text{ wt.}\% \text{ Sc}_2\text{O}_3$ ,  $\leq 2.84 \text{ wt.}\% \text{ ZrO}_2$ ; Novák *et al.*, 2008), is another mineral, which underwent partial recrystallization. It is partially replaced by fine-grained mixture of various minerals including Nb-wolframite, W-columbite, Nb-rutile, scheelite and pretulite-zircon solid solution. The pretulite-zircon solid solution contains 0.09-0.77 apfu Zr, 0.89-0.22 apfu Sc, 0.005-0.066 apfu Y, 0.001-0.029 apfu U and Zr/Hf 40. Similar solid solution was also described from epizonal metamorphosed sedimentary iron ore by Moëlo *et al.* (2002). Zr-rich compositions

tend to have increased concentrations of Y and U, indicating better solubility of large ions in zircon, than in pretulite structure and they also show elevated amounts of Ca, Al and Fe, low analytical totals and deviations from ideal stoichiometry, which are all signs of metamictization and hydration.

Composition of secondary zircon-group minerals from Dolní Bory (zircon, xenotime-(Y) and pretulite), which formed by recrystallization of different precursors is influenced by composition of their precursors and redistribution of elements between recrystallization products. Xenotime strongly prefers larger cations (Y, U, REE), whereas zircon prefers smaller ones (Zr, Hf, Sc).

In the assemblage of primary Y-rich zircon, the pretulite contains higher amounts of Y and REE, than secondary zircon and secondary xenotime is the main host of Y, REE and U.

On the other hand, in the assemblage of primary wolframoixiolite, no secondary xenotime is present because of low initial concentration of Y. In absence of the secondary xenotime, Y, REE and U are hosted in Zr-rich compositions of the pretulite-zircon solid solution, which therefore have higher concentrations of these elements than Sc-rich ones.

Our data also supports the existence of complete solid solution between pretulite and zircon, as proposed by Moëlo *et al.* (2002).

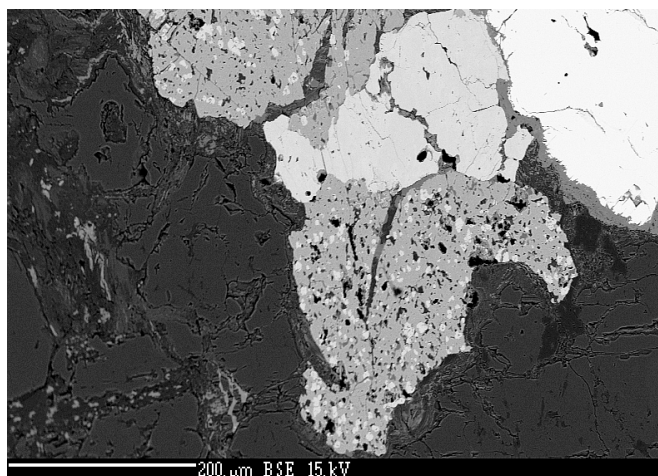


Fig. 1: Recrystallised zircon full of pores and inclusions of xenotime and pretulite. It is associated with homogenous primary xenotime (medium grey) and monazite (bright) partially replaced by crandallite. BSE.

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## Carpathian Flysch from Wadowice – history and perspectives of research

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Wadowice is a town located in the southern part of Poland, approximately 50 km from Cracow. Over one hundred years ago –in 1894– the famous Polish micropaleontologist Józef Grzybowski carried out microfaunistic research on some deposits from this area. Also the earliest practical applications of Micropaleontology in the field of Petroleum Geology were carried out by Józef Grzybowski. He is considered, by many scientists, as “the father of applied micropaleontology”. Grzybowski also described a lot of new species of foraminifera. Due to his initiative, the micropaleontological laboratory was founded at the Jagiellonian University in 1912 (Kaminski *et al.*, 1993).

Geologically, the Wadowice area belongs to the Outer Carpathians, and are built mainly by deposits of the Subsilesian Nappe. The Oligocene menilite shales and sandstones with cherts dominate in this area. Recently, during road works some of these deposits have been exposed in the vicinity of “Czumówka” estate in Wadowice. This new outcrop is located about few dozen meters from the place which was the subject of Grzybowski’s research.

In 1893, thanks to the initiative of dr J. Daniel –a wealthy lawyer, citizen of Wadowice– digging began on an exploration shaft in search for coal. In the following year, after reaching the depth of 84 metres, the further work was abandoned as the coal was not found. Samples of the recovered material during the digging work, collected by Henryk Walter, were sent to the geological cabinet in Cracow to Józef Grzybowski for micropaleontological analysis. The profile compiled by Grzybowski consisted of the following strata (from bottom to top): menilite shales, black bituminous shales, red clays with white sandstones, gray claystone with white marl and green clays, and thin layers of sandstones and sandy shales. This exploratory coal shaft was located near the place known as “Daniel’s Garden”. Unfortunately, its site is difficult to be precisely point out nowadays.

The results of Grzybowski’s studies were published in 1896 in one of his well known scientific papers “Foraminifera of the red clays from Wadowice”. In the examined samples both, the agglutinated and calcareous foraminifera were present. According to Grzybowski most of the agglutinated forms represented deep-sea species, thus the analysed deposits were considered to be of deep-water origin. In his opinion taxonomic composition pointed to Oligocene age of the studied microfauna. Of the 112 taxa of foraminifera, illustrated by him, 55 were described as the new

species (Grzybowski, 1896). It was the great achievement, not only for Polish, but also for the world micropaleontology.

A few decades later, the Wadowice area was the subject of research by Professor Marian Książkiewicz. Based on the study of H. Hiltermann (vide Książkiewicz, 1951) he suggested that the microfauna, described by Grzybowski, indicated rather Late Cretaceous or Paleocene than Oligocene. In 1981, the revision of Grzybowski’s collection from Wadowice was published by Mr. and Mrs. Liszka. These authors concluded that red clays were Campanian in age, whereas green shales and marls Paleocene (Liszka & Liszkowa, 1981).

After over one hundred years since Grzybowski’s research it is possible to examine deposits, presently exposed in the outcrop described, that seem to be similar to those recovered from the 19<sup>th</sup> century exploratory shaft. The main purpose of my research is to compare the foraminiferal assemblages with those described by Józef Grzybowski and also to determine stratigraphic affinities of the exposed strata on base of their lithology and character of foraminiferal assemblages.

Study of a new outcrop in Wadowice is a chance for more precise recognition of the local geological structure, in the nearby future. Then aim of research is a comparison between teams of microfauna from new outcrop and foraminifera described by Józef Grzybowski. Moreover, the aim is also to determine stratigraphic affiliation of rock layers. Based on the preliminary examination of profile in Wadowice can be concluded that the layers lays different to these from 19<sup>th</sup> century exploratory shaft (from bottom to top of profile lays: black shales, sandstones and menilite shales; without red clays). The recent outcrop have approximately 5,5 m high and contains generally of black shales, sandstones, grey marls and menilite shales. Collected 20 samples, in most from layers of shales, marls and menilite shales. To extract the foraminifera from samples were used method based on heating and freezing rocks.

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# Cathodoluminescence textures of hydrothermal vein quartz from the Mokrsko gold deposit, Czech Republic

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The thesis is focused on describing hydrothermal mineralization events, which created the largest gold accumulation in the Bohemian Massif - the Mokrsko gold deposit. Mokrsko is situated in Central Bohemia, about 50 km south from the city of Prague. The deposit can be described as a near-surface, low-grade (2 ppm of Au) gold deposit, hosted by a contact zone of a Variscan granitoid pluton (the Sazava granitoids) and a Neoproterozoic volcano-sedimentary complex (the Jilove Belt). Despite its being an undeveloped deposit (mining project), an extensive exploration activities (35 km of drillholes, 8 km of underground galleries) were undertaken here between the years 1980-1990. Extent of the exploration and the accessibility to its results provides ideal conditions for further research. Total gold potential was calculated on 100 tons of gold, which ranks the Mokrsko deposit among the most important gold deposits in Europe (Moravek *et al.* 1989).

SEM-CL, LA-ICP-MS, EMPA analysis of ore-bearing quartz are widely used methods in studies of mineral deposits (*e.g.* Rusk 2012). Combination of cathodoluminescent response and trace elements analysis helps us to describe different quartz generations (stages), their genesis, relationships and associated mineralizing events. Only few new studies (Zacharias *et al.* 2014; Boiron *et al.* 2001), using a combination of modern analytical methods and a present knowledge about characterization of gold deposits, were carried out here since the end of the exploration works. It is important to note that the combined analyses of CL and trace elements incorporation in quartz were not done at the Mokrsko gold deposit, as yet.

The first analyses indicate that the Au-bearing hydrothermal veins contain several quartz stages. SEM-CL clearly shows the different quartz stages in hydrothermal veins. These textures were observed in both older thicker quartz veins (Fig. 1.) and younger sheeted veins/veinlet system. We can distinguish Q1 - very dark grey to none CL (dark blue in coloured CL), which is sometimes overgrown by or alternate with bright Q2 (bright yellow in coloured CL). The last and the youngest quartz generation is grey Q3 cobweb, which cuts earlier Q1 and Q2.

As a preliminary result, it is possible to say, that heterogeneous features (representation of different quartz stages) in hydrothermal vein quartz increases toward the west (direct to the Sazava granitoids). Further work at this thesis will include geochemical analysis of trace elements incorporation in vein quartz (LA-ICP-MS and EMPA analysis), distinguish different quartz stages by their geochemical composition, relationships with mineralizing events and discuss these results with published and described genetic model/type of the Mokrsko gold deposit.

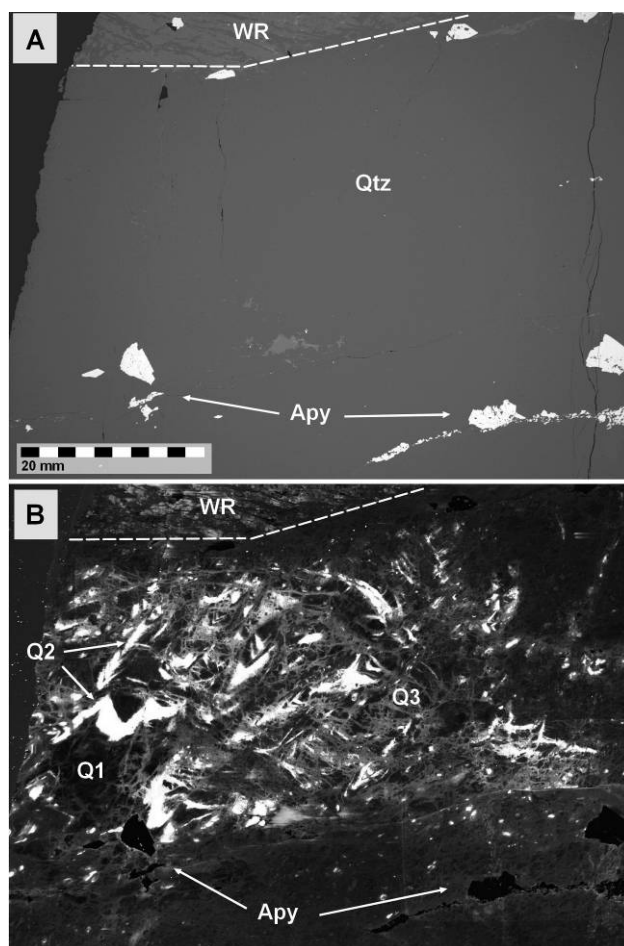


Fig. 1.: BSE (A) and CL (B) image of thicker Au-bearing quartz vein from the westernmost part of the Mokrsko-West deposit (WR - wall rock, Qtz - quartz, Apy - arsenopyrite, Q1-3 - different quartz stages).

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## Biotites of the outer fenitization zone rocks of Chernigov carbonatite complex

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The object of the study is biotites from crystalline rocks of the eastern part of Chernigovka carbonatite complex fenite halo, Ukrainian Shield (the well № 968).

The goal of the study is to detect the place of biotite in metasomatic sequence of crystalline rocks changes of the complex frame and the nature of possible changes of its optical parameters depending on the intensity of metasomatic processes.

The solved problems were to analyse the optical spectra of biotite absorption from gneisses, composite gneisses and biotite-amphibolitic crystalline schists and analyse their composition, to calculate possible crystallization temperatures by monomineralic biotite geothermometer and using petrofabric studies to reveal mineral paragenesis and the interrelation of minerals that accompany the emergence of biotite.

Petrographic studies by signs (Lukiyenko *et al.*, 2008, Passchier *et al.*, 1996) revealed at least three tectonic events, which were reflected on the formation of the mineral composition and structure of the crystalline rocks of the frame in the outer frame of the Chernihivka carbonatite complex. The earliest event is shown in intergranular recrystallization of rock-creative minerals of primary crystalline rocks, which can be granodiorites, tonalites and diorites with the creation of the corresponding composition tectonic gneisses and crystallization in the planes of recrystallization of oriented prismatic crystals and chains of hornblende and clinopyroxene. The second event, that is recorded, is the emergence of new paragenesis, which is lattice microcline and biotite, which are usually around magnetite as the reactionary mineral. At this stage which has passed in the mode of the brittle deformation with the sliding and the formation of cracks and voids, cataclasites get soaked with metasomatic fluids of potassium silicon nature and form impregnates of quartz potassium feldspar composition with diaphthoritic partial replacement of primary minerals into secondary ones: transformation of plagioclases to potassium feldspar, biotite recrystallization and regeneration, formation of blue-green and colorless amphibole in hornblende, pseudomorphic replacement of clinopyroxene by celadonite. The third tectonic event on the level of greenstone conversion is chloritization of mafic minerals, epidotization and sericitization of plagioclases, fulfillment of cracks by calcite.

Formation of biotite is associated with the first and second tectonic events. The first generation is represented by separate flakes or intergranular packages of small flakes that are hardly deformed. In all the above varieties the biotite ferruginosity is almost identical and by the correlation of formula coefficients of magnesium and iron it allows to refer them to the transitional species between annites and phlogopites with low iron content ( $K_{Fe}=0.30-0.35$ ). The second generation differs only by the morphology of the crystals and relatively small low content of titanium which is reflected in the decrease of the calculated parameters of possible crystallization temperature (Luhr *et al.*, 1984) in the most K-feldsparized varieties.

Studying of biotites optical spectra shows, that with the increasing of kalifeldsparization level of rocks the biotites overall light absorption level decreases and it is the most notable in the field of 720 nm (transition of  $Fe^{+2} \rightarrow Fe^{+3}$ ) as a result of lowering of oxidation degree of its crystallization environment (Taran *et al.*, 2013).

The conducted studies have shown that the outer zone of the fenite halo around the alkaline and carbonatite bodies of Chernihivka complex is characterized by impregnation type of silicon potassium metasomatic transformation of crystalline rocks frame. Biotite, the formation of which accompanies this process, is characterized by low ferruginosity and relatively reduced level of light absorption including the range of 720 nm, that together with petrographic observations suggest a restorative nature of metasomatic fluids. The gradient of crystallization and recrystallization temperature of biotite is 100°C and is embedded in a range of 640-540°C.

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## Evaluation of possible tailings' seal failure within Dniprodzerzhynsk industrial agglomeration (Ukraine) on the basis of the neotectonic data

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The study area is located within Dniprodzerzhynsk industrial site in the Dnipropetrovsk region of Ukraine. At this place, since 1949 to 1991, State Industrial Enterprise «Pridneprovskiy Chemical Plant», was one of the largest metallurgical facilities where uranium ores were processed. When the enterprise stopped its activity, seven tailings and two storages of uranium waste were formed on the territory and beyond. At present, about 42 million tons of waste with total activity  $3.2 \times 10^{15}$  Bq (86,000 Ci) is accumulated in tailings (Verkhovtsev *et al.*, 2010).

Neogeotectonic study of this area allows determining the degree of influence of recent activity geostructures features and their activation on rock properties (physical, mechanical, filtration and others) on which objects of study are located. Therefore it allows identifying the possible direction of migration of radionuclides and toxic compounds in groundwater aquifers and mines.

Neotectonic mapping was made on the basis of morphostructural methods in a scale of 1:25 000 (Yuskiv & Verkhovtsev, 2013).

21 lineament zones (LZ) were identified by the group of researchers. These zones are ranked as regional and local. Lineaments form two dominant systems – orthogonal ( $0^\circ \pm 90^\circ$ ,  $\pm 5^\circ$ ) and diagonal ( $40-45^\circ \pm 310-315^\circ$ ), two intermediate diagonal systems ( $25-30^\circ \pm 295-300^\circ$ ;  $74-80^\circ \pm 345-350^\circ$ ) and one depressed area ( $15-20^\circ$ ) with single lineament zone (Fig. 1.) were identified.

12 ring structures (RS) active on the latest stage (Late Pliocene–Quaternary) were allocated: nine inherited, two non-inherited and one intermediate morphogenetic types. Their sizes are from 3936x2198 m to 10474x7678 m, and the estimated (calculated) depth – from 1158.4 to 5237 m.

Analysis of summary amplitudes late Pliocene–Quaternary vertical crustal movements shows that within the study area they have differentiated and highly significant intensity (maximum values exceeding +95 m).

Definition of influence identified active geological structures on the safety of uranium tailings production, prediction of places of active absorption of polluted water by neotectonic data. The most dangerous areas are allocated in combination with the neotectonic parameters: the presence of LZ (active on the neotectonic stage of faults development), the presence of local, usually positive RS; coincidence with LZ and positive RS local anomalies of summary amplitudes increased values.

Tailing “Dniprovsk” is located in a dangerous place by neotectonic criteria. It is confined to the node intersection of three LZs: №3, №11 and №16. Especially dangerous zones are №3 and №11 because the migration of contamination is supposed by them (to the north and north-east). The RS №2 and 3 affect directly at the tailing as it is located at their peripheral parts. At the same time, by vertical movements, it is a relatively quiet place and characterized by summary amplitudes of +5 m or less.

Tailing “Zakhidne” and “Central Yar” are located directly within the local LZ №3 and №3 RS, and they are probably the ways of active contamination migration.

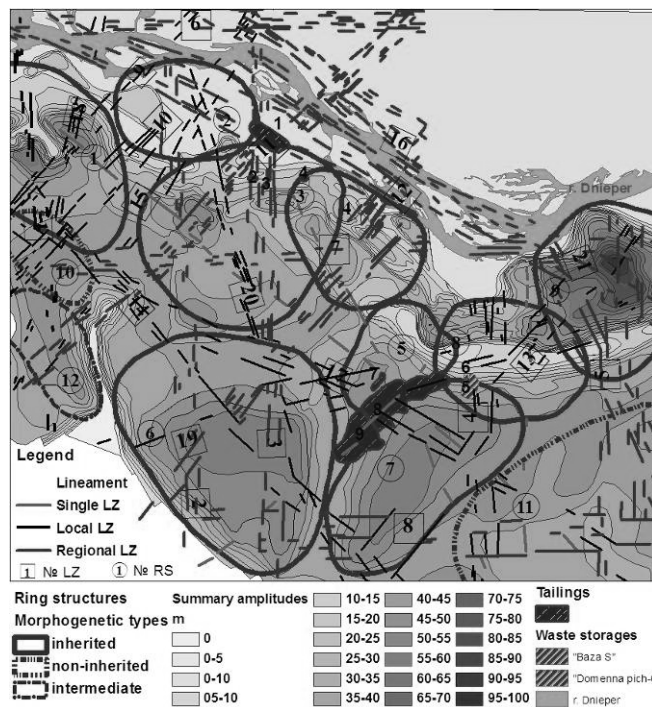


Fig. 1. Neotectonic map of the territory of uranium production legacy site at Dniprodzerzhynsk (Yuskiv & Verkhovtsev, 2013). Scale 1:25 000 (reduced).

Legend: Tailings and waste storages of uranium production:

- 1 – «Dniprovsk», 2 – «Zakhidne», 3 – «Central Yar», 4 – «Pivdenno-Skhidne», 5 – «Baza S», 6 – «Domenna pich-6», 7 – «Lanthanum fraction», 8, 9 – «Sukhachivske» (1<sup>st</sup> and 2<sup>nd</sup> sections).

Tailing “Pivdenno-Skhidne” is located in the best neotectonic conditions.

The rise of radionuclides migration is assumed on the territory where the tailings “Lanthanum fraction”, “Sukhachivske” (1<sup>st</sup> and 2<sup>nd</sup> section), “Domenna pich-6”, “Baza S”. It is caused by the influence identified LZ №4, 17, 19 and the erosion form associated with the tailings. Tailing “Sukhachivske” is framing at RS №7 and a crossing is also observed at RS №5, 8, 7. Average summary amplitude by height is +40-50 m, so they, presumable, have some minimal impact.

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## On the veinlet-impregnated mineralization in terrigenous strata of the Krosno zone (Ukrainian Carpathians)

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Veinlet-impregnated mineralization is widely distributed in the rock complexes of the Carpathian petroliferous province. It is the consequence of healing fractures formed in the process of formation of great overthrust structures under the influence of the drifting Pannonian plate in the direction of the East European Platform (Vyalov *et al.*, 1981; Matvienko & Naumko *et al.*, 2004). It is mainly represented by quartz and calcite with admixtures of barite, dolomite, pyrite, halite, gypsum and other minerals (Naumko, 2006). Calcite veins, veinlets and impregnations in the terrigenous deposits of Ukrainian Carpathians are saturated with oil bitumens (in exposures) and oil (in oil fields) noticeably. Regardless of the age of rocks in which they occur (from Cretaceous to Paleogene), the time of the formation of the veinlet-impregnated mineralization is dated as Post-Paleogene (Rypun, 1971).

Significance of its studying within the limits of the Krosno Zone, which is promising for oil and gas (Krupskiy, 2001), is defined by that it can testify to the influence of deep-seated processes in the course of processes of synthesis, genesis and migration of hydrocarbons and their localization in deposits (Naumko, Bekesha, & Svoren, 2008). With that end in view we have studied the veinlet-impregnated mineralization of vein formations in natural exposures of this zone, in particular the Volosyanka, Pre-Duklya, Yavoriv, Lower- and Upper-Turiv and Borynya scales of the Bitlya subcover and the Yabluniv, Ropavske, Limna, Shum'yach-Zavadiivka and Gronzyovo scales of the Turka subcover using mineralogical, X-ray powder diffraction and fluid inclusion thermometric methods.

Veins and veinlets fill up ruptures or shear fractures, are deposited on the walls of rock-forming minerals in the form of touchings and hubs. They are mainly subparallel, sometimes of different orientation, often pinched out. The thickness of veins and veinlets is estimated to range from microscopic to over 55 mm.

According to data of mineralogical observations and X-ray analysis it was established that veinlet-impregnated mineralization is mainly represented by calcite with the traces of quartz.

Calcite occurs as granular dense aggregates, druses, sometimes well-faceted crystals (Borynya scale). The size of grains varies from fine-grained (0,1 mm) to coarse-crystalline (4-6 mm).

Crystals are mainly of rhombohedral, prismatic and scalenohedral habit with well-expressed facets of rhombohedron  $\{10\bar{1}0\}$  and  $\{01\bar{1}2\}$ . On the facets one can often observe growth hatching and cleavage. Cleavage is eminent along the rhombohedron.

The colour of calcite is mainly milky-white, tinted by admixtures of different light colours (grey, yellow), sometimes limpid individuals are also found.

There are two calcite generations. Calcite of the 1<sup>st</sup> generation is coarser-grained, semi-transparent tinted with yellowish, and calcite of the 2<sup>nd</sup> generation is opaque, of milky-white colour. X-ray analysis has allowed us to determine insignificant differences in the intensities of calcite of different generations. This can testify to change in the intensity of display of fluid-saturation of migratory mineral-forming fluids.

Inclusions in calcite are located in the healed fractures and along cleavage planes (the latter are predominant).

By the phase composition these are one-phase liquid and two-phase – gaseous-liquid. Flat inclusions of irregular form predominate, extended and rectangular ones are present as well. Some vacuoles have a stepped development of the walls that is characteristic of carbonates. In all samples the phenomenon of inclusions unlace is found. Their size is estimated to range from 0.01 to 0.001 mm.

The most widely distributed temperatures of homogenization of fluid inclusions according to data of thermometric analysis are 170-220°C that correspond to conditions of maximum temperature of preservation of hydrocarbons in the Earth's crust regardless of their origin (Naumko, 2006). The latest inclusions are homogenized at temperatures from 80 to 105°C. Intermediate value of homogenization temperatures is 135°C.

Results of our investigations show that veinlet-impregnated mineralization, which is widely distributed in deposits of the Krosno zone of Ukrainian Carpathians, is essentially of calcitic composition, but calcite heals migration fractures in terrigenous strata that cannot be a single source of calcium for the formation of veins, veinlets and impregnations of calcite.

According to data of Svoren & Naumko (2009), the source of Ca<sup>+</sup> for the formation of calcite of veinlet-impregnated mineralization is deep-seated high-temperature fluid in the composition of which CaO, CO<sub>2</sub> and CH<sub>4</sub> below 580°C form a “lime milk”. This mixture of CH<sub>4</sub>, Ca(OH)<sub>2</sub>, CO<sub>2</sub>, steam – compounds with low coefficients of internal friction migrates at a great distance, in particular in a form of Ca(OH)<sub>2</sub>·CH<sub>4</sub>, and fills pores, cavities and fractures with the “lime milk”.

On decreasing temperatures, they are healed with carbonates that capture relicts of the carbonate-forming medium in the form of inclusions together with methane (and other hydrocarbons).

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## Brachiopods from the Upper Ordovician Mežciems Formation from eastern Latvia

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Several deposits of marine facies zones, which vary both in composition and sedimentary environment, can be traced throughout the Baltoscandian territory. Large sections of the Ordovician in the modern day territory of Latvia change in the lateral aspect, where the north-western facies belt differs significantly from the south-eastern belt. Type section correlation is therefore a relevant issue, which can be solved by studying fossils and the subsequent correlations. The aim of this study is to determine and classify several brachiopod genera which are intrinsic to the Mežciems Formation, in order to refine, reconstruct and understand what the conditions were like, for example, sea level or depth of the paleobasin, during the afore mentioned time. This study will also improve the basis on which the Mežciems Formation can be further subdivided into members, and its stratigraphic borders in Eastern Latvia.

During the Ordovician period, the position of the Baltic paleocontinent moved from around 40-50° south, to a position very close to the equator. The territory of modern day Latvia was located in the central part of the Baltic paleobasin (Hints & Harper, 2003) with land surrounding the Baltic gulf from the west, north and east. Sea levels range from deep sea to littoral zones due to several sea transgressions and regressions. The stratigraphy of the Ordovician is almost complete in Latvia – an exception being in the Valmiera-Lokno region, where there are no Ordovician deposits. In general, Ordovician deposits in Latvia are mainly carbonate, due to the warm climate conditions, but marlstones, clays, dolomites, mudstones, argillite, sandstones and siltstones are also common. In the Upper Ordovician, the most common limestone deposits are various types of micrite, wackestone, grainstone as well as oolitic limestone, biosparite and, the most important, fossiliferous limestone. During the late Ordovician it is thought that the deepest sea depths were in the western Latvia region, with shallower waters in the east (Dronov *et al.*, 2011). In western and central Latvia, upper Ordovician deposits consist of limestone, marlstone and mudstone (argillite) and clay. Conversely, upper Ordovician deposits in eastern Latvia contain limestone and marlstone layers with undulated layered marlstone interbeds (~60% of the total Ordovician section), marlstone with lenticular limestone inclusions and biomicrite/sparite, which consist mainly of remains of brachiopods, trilobites, corals and other fauna and flora (Brangulis *et al.*, 1998).

The Mežciems Formation is distributed only in eastern Latvia – its equivalents in western Latvia are the Mossen, Blīdene and Adze Formations. The Mežciems Formation spans the Haljala, Keila and Oandu regional stages. In total there are 9 drill-cores where the Mežciems Formation is confirmed (see fig. 1.). Only 5 of these drill-cores are currently being studied and the contained brachiopods classified up to the genus level. The typical deposits of the Mežciems Formation are grey, undulating layered detrital and biomorphic clayey marlstones, as well as limestone with thin metabentonite layers, with ostracod, brachiopod and chitinozoan remains (Anikejeva, 1997).

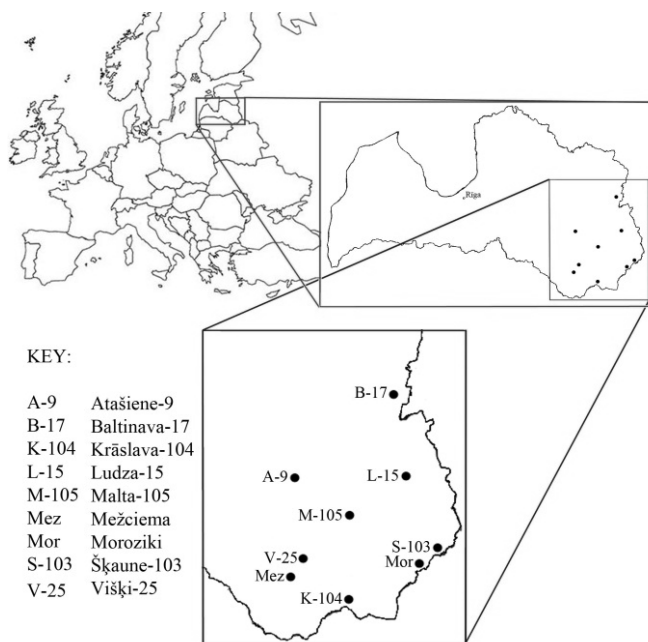


Fig. 1.: Location of drill-cores with confirmed Mežciems Formation.

Through research of papers, such as: Ulst *et al.* (1982), Paškevičius, (2000), and others, it has been determined that the following brachiopod genera are intrinsic to the Mežciems Formation and its equivalents in neighbouring countries: *Dalmanella*, *Howellites*, *Orderleyella*, *Platystrophia*, *Neoplatystrophia*, belonging to the order Orthida; *Porambonites* and *Nicolella*, order Pentamerida; *Sowerbyella*, *Longvillia* and *Leptaena* of the order Strophomenida; and finally *Vellamo*, which belongs to the order Billingsellida. Currently, the dominating genera in three of the drill-cores are *Sowerbyella*, *Dalmanella*, *Howellites*, and slightly less abundant, *Platystrophia*. A change over between the *Sowerbyella* and *Howellites* is noted in all of the drill-cores, where one genus “replaces” the other, but an unequivocal border has not yet been defined.

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## Formation conditions of the veinlet-impregnated mineralization in Paleozoic deposits of the Lviv Depression (the West of Ukraine)

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Because of the rise of demand for energy carriers worldwide, the usage of unconventional hydrocarbon (HC) raw materials, first of all such as HC gases of the gas-oil fields and “shale” gas of the black shale formations is a vital problem. One of such regions is the Lviv Paleozoic Depression included in the Volyn-Podillya petroliferous area (Dolenko *et al.* 1985). This is confirmed by the discoveries of the Velyki Mosty and Lokachy gas fields in the rocks of the Lower and the Middle Devonian. At the top of the section, in the Carboniferous coal-seams, the Mezhyrichchya gas-coal field is located and Silurian rocks, occurring stratigraphically below, are promising for “shale” gas deposits (Naumko *et al.*, 2013).

Therefore, it is important to study the volatiles of fluids owing to which the formation and transformation of deposits of prospective gas-bearing sections of the region occurred (Naumko, 2006). Volatiles have a great influence on the processes of minerogenesis. It was their regime that determined the intervals of the fluid’s functioning, the parameters migration of their components, and their disintegration under definite physical-chemical conditions promote developing of the phenomenon of heterogenization that leads to the change of such important parameters of the fluid medium of the mineral crystallization as an aggregate state, a concentration, acid-alkali and oxidoreductive indications.

According to Zinchuk *et al.* (2002), the formation of veins and veinlets in the deposits of the Lviv Paleozoic Depression is connected with catagenic and post-catagenic processes. The earliest Carbonate concretionary formations are represented by siderite, sideroplesite and ankerite, with dissemination of pyrite. The veinlet formations in rocks of the Upper Devonian are represented by the veinlets of milk-white and grey calcite, often with admixture of pyrite about 20 mm thick. Veinlets of anhydrite-calcite composition, veinlet-like secretions of greenish hedromica and pyrite are found not often. In secretions of the Devonian D<sub>3</sub><sup>1</sup> in the area of Verbizh, a vertical veinlet of anhydrite 10 mm thick was found, along borders of which a thin edge (1.5 mm) of zonal rhombohedral crystals of brown dolomite are developed, on which later quartz, rarely scalenohedral calcite, pyrite, sphalerite grew.

The multistage character of veinlet mineralization as well as its polygenetic nature indicate, the coal genesis of a part of gases, and the influx of methane included in the deep-seated high-temperature fluid (Naumko & Svoren, 2003) through oil-conducting dislocations like the Belz-Mylyatyn fracture (Kalyuzhnyi *et al.*, 1975).

Two trends of evolution of HC systems were established: a) vertical zonality: transformation into oil-like mixtures and bitumen-like liquids and solid bitumen due to loss of volatiles; b) lateral zonality: substitution of oil-like mixtures for light essentially methane fluids (Zinchuk *et al.*, 2003).

In the Lviv Paleozoic Depression, the following types of HC-water inclusions were identified in Devonian and Carboniferous deposits: oil-like mixtures – one- and two-phase, with homogenization temperatures of 30–128°C and syngenetic with inclusions with drops of yellow oil; inclusions of liquid and gas-like

mixtures of volatile HCs with predominance of methane of gas-condensate type; two-phase inclusions of brown and red-brick bitumen; one-phase inclusions of supercritical methane of high density (Zinchuk *et al.*, 2001). The temperature of fluid environment was not lower than 160–200°C. On condition of rising movement of fluids it fall 15–20°C per 100 m (Kalyuzhnyi *et al.*, 1975, Zinchuk *et al.*, 2003).

Based on methane predominance (up to 100 vol. %) and the appearance of ethane (first %) at deeper horizons in volatile of fluid inclusions in minerals and closed pores of graptolite argillites of Silurian of the Lviv Depression, conclusions (Naumko *et al.*, 2009, 2013) about the availability of conditions for the gas forming processes by a way of transformation of the organic matter into “shale” gas were drawn. The absence of steam testifies the “dryness” of the HC-containing system and low values of the gas saturation testifies the transformation of the organic matter under low (mainly lithostatic) pressures. At the same time, an order of magnitude higher relative gas saturation of veinlet calcite with which subvertical fractures in the argillite strata are healed and the appearance of steam indicate the possible influx of the deep-seated migratory paleofluids.

Thus, the fluid phase that was formed under the influence of deep-seated factors (Naumko *et al.*, 2009) interacts with the rocks and changes their paragenetic associations. This promotes determining of the equilibrium in the system rock-external physical-chemical parameters (pressure, temperature). This causes the importance of further investigations of the deep-seated and sedimentary HC fluid systems based on fluid inclusions with the purpose of determining parameters of migration processes within the limits of the Lviv Paleozoic Depression emphasizing the methane (HC) specialization of fluids.

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# Petrography and Sedimentology of Lower Triassic siliciclastic sediments in Giewont Unit, Tatra Mts.

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Tatra Mountains are a part of the Inner Carpathians. They contain a crystalline core and a Mesozoic sedimentary cover. Tatra Mountains are divided generally into three tectonic-facies units – Tatricum, Fatricum and Hronicum. The studied sedimentary rocks are found in the Tatricum Unit, exactly in the subunit of Giewont, which contain a part of the crystalline core and a Mesozoic sedimentary cover from Triassic to Cretaceous.

The sediments, which were studied, are found in central part of the Tatra Mts. The outcrop is located south of the Giewont Peak. It comprises a profile of siliciclastic rocks, which are located directly on the crystalline core. The boundary between magmatic and siliciclastic rocks is not visible in the field. The studied sediments are of Lower Triassic age, exactly Seis (Sokołowski, 1948). The specific research of the petrography of sediments was made. In the lower part of the lithological profile, conglomerate with lithoclasts of quartz and magmatic rocks are found. Then a change of the facies was observed. The size of grains decreased. In the middle part of the profile reddish and greyish sandstone is located. The highest part of the outcrop comprises sandstone with thin layers of red and green mudstone.

In the outcrop fossils and bioturbation structures were not observed. The red and the green mudstone do not contain organic matter also. In the lower and middle parts of the lithological profile, cross bedding was observed. Some of the ceilings of the beds in the lower part are covered with ripplemarks. They are helpful marks during the interpretation of paleoenvironment of Lower Triassic in the Tethys Ocean.

The topic of the paleoenvironment of these sediments is still discussed. The interpretation was changing through years. Nowadays, it is claimed that the conglomerate and the lower part of reddish and greyish sandstone were embedded as sediments of a braided river. In the upper parts of the Seis profile, the facies changed into shallow-marine sediments (Passendorfer, 1950).

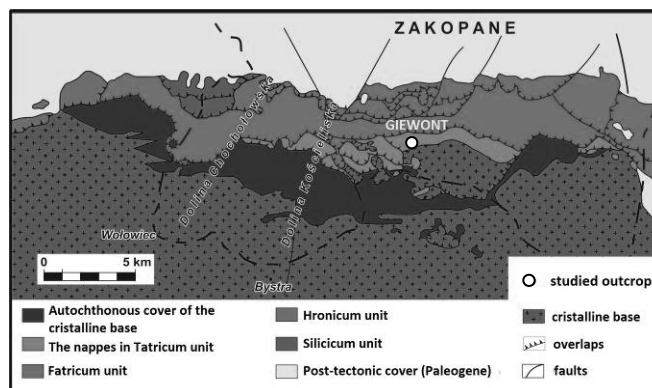


Fig. 1.: Tectonic map of the Tatra Mountains marked with the studied outcrop.

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